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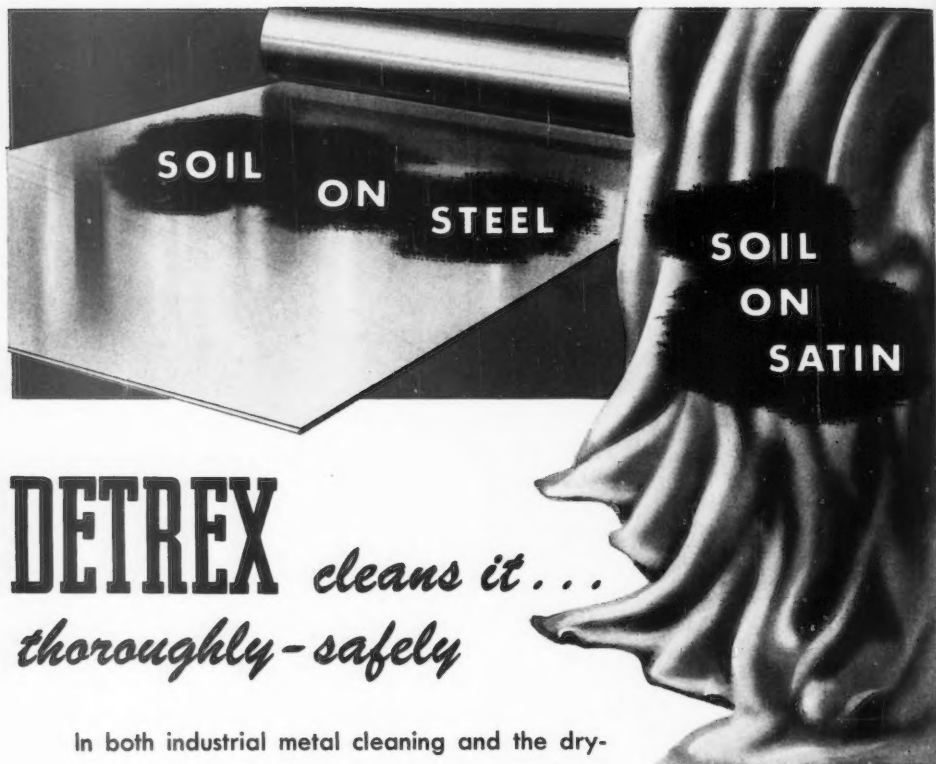
*Industrial*  
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*Quarterly*

VOLUME 18, NUMBER 2

JUNE, 1957



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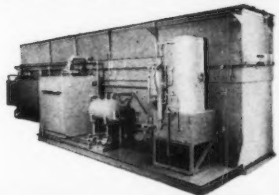


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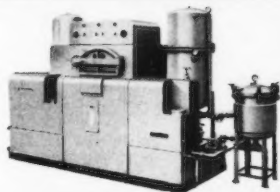
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ASSOCIATION

## Quarterly

Volume 18

JUNE, 1957

Number 2

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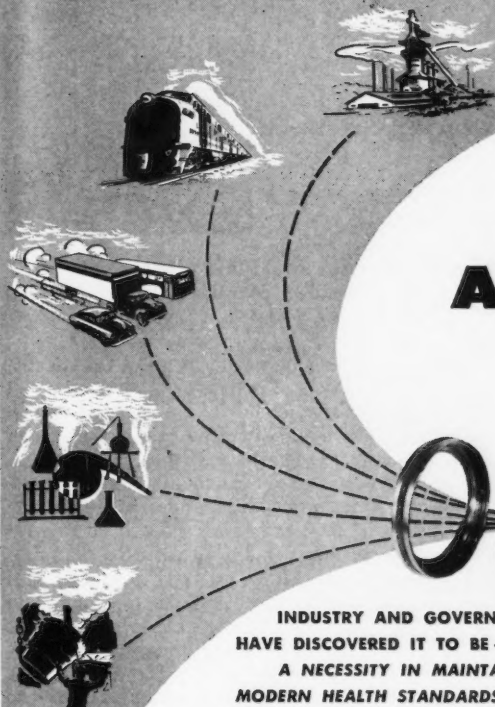


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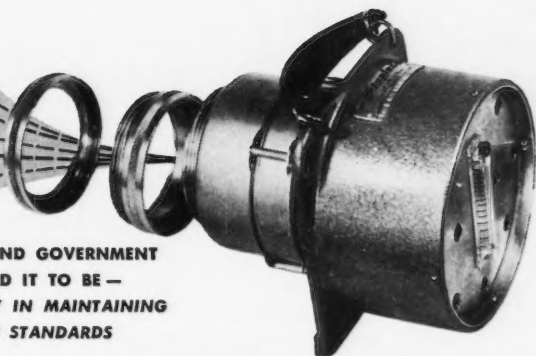


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## ◆ President's Page



FOR NEARLY two years, committees of our Association have been studying problems related to certification and registration of industrial hygienists. There has been considerable confusion among our members on these two subjects. They are actually quite different.

Registration is carried out by a governmental agency (state or municipal) for the purpose of controlling the practice of certain professions which may affect the health or safety of the public. Certification, on the other hand, is a means of maintaining high professional standards. It is generally set up by some competent, well-recognized, self-appointed group. This group sets up a certifying board which establishes criteria for evaluating competence and certifies members who qualify. Certification of industrial hygienists then could be done by our Association.

Interest in such action has been stimulated by an invitation to AIHA to have representation on the American Sanitary Engineering Intersociety Board for the purpose of certifying industrial hygiene engineers in the sanitary engineering field. It is noteworthy that several AIHA members who are prominent in the engineering field are already taking active part in this endeavor. It is also pertinent that the American Public Health Association is now represented on that board. There is no reason why individual qualified engineering members of AIHA should not be certified under A.S.E.-I.S.B. The deadline for such certification without examination is October 1, 1957.

This move toward certification of industrial hygienists in the engineering field has caused a considerable stir among our membership, chiefly because of misunderstandings. It is my hope that through a series of discussions on this page it will be possible

to clarify the situation so that members will be in a position to act wisely when called upon to make decisions about these matters.

FIRST it must be borne in mind that AIHA is composed of a large number of what might be called minorities. There is no majority. We are made up of many disciplines—chemistry, physics, toxicology, medicine—and even greater refinements such as meteorology, acoustics, etc. Under these circumstances it is going to be difficult to provide for certification in the broad field of industrial hygiene. It is entirely probable that various segments of our membership will become involved in certification within their own specialty. This, of course, is already true in the medical and engineering fields. One decision which will ultimately have to be made is whether AIHA should favor having its members become certified in their special fields as in the case of engineers and physicians or whether an attempt should be made to provide broad certification in industrial hygiene with designated specialties, such as Industrial Hygiene (Toxicology), Industrial Hygiene (Chemistry), etc. A third alternative is to encourage both. Our committee on certification is studying these and many other phases of the problem. Since this ultimately will involve an important policy matter, their recommendations will be submitted to the entire membership for decision.

Your suggestions and ideas in this matter are earnestly solicited. They should be sent to Dr. Lewis J. Cralley, Chairman, AIHA Ad Hoc Committee on Certification.

*Charles R. Williams*



# Growth and Progress in Industrial Hygiene

## *The Donald E. Cummings Memorial Lecture*

H. H. SCHRENK, Ph.D., Research Director  
Industrial Hygiene Foundation  
Pittsburgh, Pennsylvania

A TRUE appraisal of the status of an organization or its field of endeavor should take into consideration two basic criteria—growth and progress. While these criteria may seem to be synonymous, distinctly different meanings are used in the present discussion. By growth I mean increase in routine industrial hygiene practice and increase in membership, local sections, publications of the Association and other activities which indicate physical expansion. Progress, on the other hand, is here used to refer to new developments which increase the unique and systematic technical knowledge which is the foundation of industrial hygiene activities.

One may have growth simply by adding equipment so that more analyses can be made, or increasing personnel to expand routine work. Such increases in activities are not classed as progress in the present discussion, but rather as a normal growth to keep pace with increase in industrial expansion. In fact, to remain static would indicate regression. Hence, continued extension of conventional industrial hygiene activities is necessary and is to be expected if industrial hygiene is to retain its present position.

A brief review of the growth of the American Industrial Hygiene Association will serve to illustrate the expansion of industrial hygiene practice. The membership of



our Association has grown from 160 in 1940, to over 1000 at the present time. The increase has been at a regular rate, averaging about 65 per year, and this is an encouraging sign that continued growth may be expected.

An outstanding indication of the more mature character of AIHA has been the development of the *Quarterly*. Starting as a section of a few pages in *Industrial Medicine* in 1940, it became an individual publication of some 32 pages per issue in 1946, and has become a highly respected Journal of over 450 pages in 1956. This growth of the *Quarterly* has much greater significance than mere increase in number of pages. It is, at the same time, evidence of progress because it reflects an increase in both research and development.

Another important measure of growth is the number of Local Sections, which now total 22. The Local Sections play an important role at the grass root level in expanding industrial hygiene services and demonstrating the benefits of environmental control to local industries, particularly the smaller companies.

The increased activities of the Technical Committees are further evidence of the growth of the Association. These committees help significantly in the practical application of accumulated industrial hygiene knowledge. One of the most important stimulants of growth is assimilation and utilization of the fruits of research at the earliest possible moment. This, of course,

Presented at the Eighteenth Annual Meeting of the AMERICAN INDUSTRIAL HYGIENE ASSOCIATION, St. Louis, April 24, 1957.

is not the responsibility of the committees alone, but is the responsibility of each industrial hygienist.

It is evident, then, from the viewpoint of growth that industrial hygiene and the Association have done well and it may be anticipated that a healthy growth will continue. However, my purpose is not to review our past accomplishments but to appraise future activities. It is not enough to have physical growth only; progress requires "mental" development as well. It is the research phase of our activities to which I wish to direct the major part of my discussion.

The life blood and vitality of scientific endeavors are dependent upon the caliber of the research. Future progress, as well as continued healthy growth, of industrial hygiene and our Association will rest on the expanding foundation built by research and new developments. Our strength lies in the special competence that research will provide for solving particular kinds of health problems.

The increase in expenditures for research in the United States has been phenomenal. It is estimated that less than \$200 million was spent for research in 1929 and the figure was less than \$400 million in 1940. Yet in 1955 it had reached the sum of approximately four billion. This tremendous increase becomes even more significant when it is realized that as much has been spent since 1948 as was spent in the period 1776 to 1948. This acceleration of expenditures for research is continuing.

Emphasis on research has already resulted in numerous new materials and industrial processes, with concurrent introduction of new hazards to the workers. Newer plastics, agricultural chemicals, high energy fuels, nuclear energy and automation exemplify these industrial changes. Such new industrial developments appear likely to continue at an ever-increasing pace. The creation of new materials, which after all is done for the purpose of benefiting mankind, carries with it the responsibility to make certain that the usefulness is not outweighed by risks to health. The industrial hygienist, also, has a responsibility to keep abreast of these industrial changes so that he can continue to exert leadership in coping with new problems that arise and

retain the position of pre-eminence that he has established for himself in this field.

Readjustments in our social order are being made to meet the altered conditions resulting from technologic advances. Hence, we must recognize that the viewpoint regarding acceptable working environments is undergoing change, and that steadily rising standards are being demanded. Our objective in the past has been mainly the prevention of occupational diseases by maintenance of an environment as free as possible from the conditions which lead to both physical and mental disabling illnesses. However, the worker's demand for a satisfactory working environment makes little distinction between disease and the nuisance of discomfort. The fact that man has remarkable powers of adaptability does not prevent a desire for more nearly optimum conditions. This trend toward more and more "fringe benefits" may further emphasize the nuisance aspect.

Both the technological and social changes place greater demands on the industrial hygienist to provide a working environment in keeping with present trends. Thus, our need for new tools and procedures, and new yardsticks for measuring the relative magnitude of individual components of the total problem as well as appraising the success of our efforts, becomes more essential.

#### Analysis and Instrumentation

THE ROLE of analysis and instrumentation in research probably will never receive the recognition which is its due. Nevertheless, the dependence which other disciplines in industrial hygiene place on the measurement of toxic substances and other environmental factors attests to the fundamental importance of this activity to the over-all success of our endeavors. It was Lord Kelvin who said "I often say that when you can measure what you are speaking about, and express it in numbers, you know something about it. But when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meager and unsatisfactory kind."

Increased attention to research in this phase of industrial hygiene is especially important. The fruits of such research are two-fold. First, they provide new tools and instruments directly applicable to the needs

of the industrial hygienist. Secondly, those doing research are in a position to keep abreast of new developments in the general fields of analysis and instrumentation and to apply the newer developments to industrial hygiene with a minimum of delay.

An excellent example of progress in the analytical field is the spectacular advance in gas chromatography in recent years. There also has been rapid expansion in absorption, emission, infrared, ultra-violet, x-ray and mass spectroscopy; fluorescence spectrophotometry, flame photometry, electro-analytical chemistry, nuclear magnetic resonance, electron paramagnetic resonance, and polarographic instrumentation. Concurrently, there have been many contributions in the more conventional analytical fields of colorimetry, titrimetry and turbidimetry.

While these instruments and procedures may not find wide application in industrial hygiene, a knowledge of these new developments is essential in the development of the more practical instruments which are in day-to-day use in the field. Even the simplest "gadget" is based on some specific chemical or physical response. While it is a far cry from the massive laboratory instrument to a detector that weighs only a few pounds, the importance of such gadgets should not be underestimated. The ability to obtain results quickly with reasonable accuracy at the site of sampling is a valuable asset in comparison with methods which require collection of sample and subsequent analysis several days later in the laboratory.

An ideal solution to the problem of measuring environmental contaminants is the use of continuous recorders. Here, too, we can draw from new developments in other fields. For example, the rapid advances in the electronics field may provide the means of making such devices less bulky, less expensive, and more reliable.

One cannot help but ponder the technical difficulties that our nuclear energy programs would have encountered if radioactive materials did not have properties which make their detection and measurement relatively simple. Would the outstanding record of health protection have been attained? Would progress have been delayed? Would the cost have been much greater to control intangibles? Even such simple devices as

the film badge, dosimeter, and Geiger counter may have played a more important role in the rapid progress in the use of ionizing radiation than is usually recognized. A film badge, or "dosimeter," to measure accumulated exposure to fluorides, lead, carbon tetrachloride, benzene and many other common industrial materials would be welcome, indeed.

The area of analysis and instrumentation is one in which industrial hygiene has far too few specialists.

### Biological Research

WHILE analytical tools are essential to industrial hygiene progress, their true value depends upon our ability to interpret the results of such measurements in terms of a quantitative relationship with harmful or objectionable effects. This in turn requires a knowledge of the biological response to offending agents. Here, again, we must turn to a quantitative basis of how much can be endured without adverse effects. Past experience and observation on the health of those who have been exposed have provided us with much information on safe and acceptable standards of exposures in industry. However, as our knowledge of less obvious effects increases, and as diagnostic procedures become more refined, we must continually reassess accepted values. At the same time, we are confronted with innumerable new materials which are being introduced into industry at an unprecedented rate.

If injurious or objectionable effects are to be prevented, some knowledge of the potential response to these materials must be obtained before they are produced in quantity. This requires experimental studies with animals. Considering the number of substances to be tested and the time required to provide meaningful data on the chronic biological effects of a single compound, the problem appears almost insurmountable.

The present experimental procedures which require several species of animals and years of exposure for chronic effects, indicate the limitation of existing methods in terms of output. Long term exposures which cover the life span of an animal become almost as much a study of animal geriatrics as a study of the biological re-



sponse to a particular substance. There is need, therefore, for basic investigations of biological procedures which might provide more meaningful information with less expenditure of time and effort. Studies which provide data on rate of absorption, distribution, metabolism, storage, elimination, latent effects, and repair of damage should lead to a much better understanding of potential biological effects than investigations concerned mainly with chronic toxicity. This is particularly true when one considers the difficulties of extrapolating the results of animal experiments to man.

The anticipated increase in the number of women and older workers in industry, and the need for more skilled workers with the introduction of automation, forecast a trend toward more attention to problems which are difficult to define. These include fatigue, emotional disturbances and adaptability to unusual stresses. Rapid advances in the medical sciences are likely to provide new knowledge and techniques that can be applied to studying the biological response to toxic materials. For example, the enzyme, cholinesterase, serves as a means of measuring exposure to certain phosphorus-containing insecticides. The effect of poisons on other enzymes should be a fruitful area for basic research. Also, the value of tissue culture studies for measuring response to toxic substances is worthy of further exploration. As our ability to measure minute changes increases, the possibility of studying changes in single cells becomes more promising. Even changes in the composition of tears may provide an index of biological response.

Valuable as they may be, animal experiments provide only a tentative standard of acceptable exposure. The final decision regarding whether the standard is satisfactory, will depend upon the experience of the workers as determined by medical supervision. The ability of the physician to measure biological response may in turn depend in a large measure on information obtained from research studies in the laboratory, particularly those pertaining to biochemical changes. Hence, laboratory studies serve the dual purpose of providing data for establishing standards and of providing better diagnostic tools for checking the reliability of those standards.

Some standardization of biological research procedures is necessary. Nevertheless, when one considers the cost and time required to assure the safe use of a single compound, the benefits to be derived certainly justify increased basic research to develop new experimental procedures.

### Engineering Control

**E**NVIRONMENTAL measurements, biological data, and clinical and physical examinations of the workers have a primary purpose, namely, to provide a sound economic basis on which to design engineering control measures and to determine if such measures are effective. The efforts of any one profession would be ineffective. Simple cooperation is not enough; there must be a cohesive force of mutual respect which forms a oneness of action to attain a common objective. It is this close relationship between the professions which has developed a unique approach and a body of technical knowledge for solving specific environmental problems that is the core of the practice of industrial hygiene.

In view of the activities of some other groups in areas of environmental problems and human engineering, it is very important that this close relationship in industrial hygiene be maintained and strengthened, otherwise encroachment from other fields will weaken our over-all progress.

### Future Needs

**T**O RETAIN its present position, it is evident that the nature and scope of industrial hygiene practice must change with progress in science and technology as well as with social trends. How can the industrial hygienist meet this challenge? First and foremost, the field of industrial hygiene must be made sufficiently rewarding, both financially and professionally, so that it will attract capable scientists from the various disciplines to devote their full time to this field. Secondly, problems in industrial hygiene should attract the attention of researchers in allied fields so that they will find it worthwhile to devote some of their special knowledge to this field. And, thirdly, industrial management must be made to recognize that control of the working environment is an essential component of plant design and operation.

To provide a continuing supply of trained personnel in industrial hygiene, more effective recruitment of persons at the graduate level is needed. Fortunately, there are now a number of graduate schools which provide excellent training programs and facilities. Increased availability of fellowships should be promoted by our Association. Such fellowships will provide an added inducement to specialization in the field of industrial hygiene. However, the basic incentive must come from a recognition of the opportunities in this field, and a conviction that dedication to a career in industrial hygiene will result in worthwhile contributions to the betterment of mankind and a sense of pride in these accomplishments for the individual. To accomplish this will require the best efforts of our Association, the teaching profession, and each individual member of both groups. The recruitment of qualified personnel is probably the most important factor in the future progress of industrial hygiene.

A nucleus of highly respected research workers devoting their full time to industrial hygiene serves a dual purpose. In addition to its direct contributions, it can attract those in allied professional fields to devote their specialized talent to problems in industrial hygiene. Ours is a field which can profit from cooperation with many professions, and forceful and imaginative leadership can play an important role in expanding research activities. In attempting to draw other professional personnel into the orbit of our problems, it need not be with the intention of changing them into industrial hygienists. Neither should it be to use their specialties simply for technical assistance. Rather, we should attempt to develop in them an industrial hygiene approach, that is, an appreciation of the significance of the problem to which they would apply their knowledge and training. In this way the chemist, the physicist, the biologist, the physiologist, the physician and the engineer may realize that research in the field of industrial hygiene may provide some of the most fruitful outlets for their talents. A problem which challenges the intellect is much more likely to receive an enthusiastic approach than one which merely requires some particular technique. Certainly, industrial hygiene should offer excit-

ing and intriguing problems to the imaginative and adventurous scientists in other professions.

Science is advancing on many fronts simultaneously, but these advances are not in individual compartmented areas. They require cross-fertilization, a new development in one field giving a helping hand to progress in another field. Basic tools such as the x-ray, electron microscope and radioactive materials are applied virtually universally in all scientific fields almost as soon as they are made available. However, there are many discoveries in one field or another which do not find their way into other fields until after long delays. By attracting researchers from other fields to challenging pursuits in industrial hygiene we derive the benefits of new developments in these fields with a minimum of delay. In this way, industrial hygiene will be enriched by new ideas and developments from allied research, and will become a more respected field for participation by others.

Probably the most difficult task that confronts the industrial hygienist is convincing management that an industrial hygiene program is an essential component of modern industrial production. One can cite a number of companies that have outstanding industrial hygiene departments and have a thorough understanding of the importance of the services rendered. The fact is, however, that the percentage of such companies is extremely low, and frequently one is astounded at the lack of understanding and recognition by some companies that there is such a thing as industrial hygiene, much less that there is a need for it.

It is frequently not recognized by industry that the successful application of a new product falls within the framework of the basic philosophy of industrial hygiene, namely, that any material can be used safely if proper controls are instituted. The controversy regarding the commercial introduction of lead tetraethyl and the fact that it has been used safely for many years is a clear demonstration of the successful application of industrial hygiene practice. There are many highly toxic substances serving useful purposes that could not be used if the means for evaluating and controlling the hazards had not been developed. Progress in development of insecticides,



plastics, synthetic fibers and numerous other materials that are widely used today would have been greatly handicapped without the guidance of the industrial hygienist.

It is not expected that the education of industry to the benefits of industrial hygiene programs will be revolutionary. Fortunately, however, there is a trend in industry to provide better working conditions. The large capital outlay required to provide production facilities for even a single worker should make industry aware of need to give consideration to those environmental factors which increase the efficiency and well-being of its employees. Machines are not productive unless operated. The advances of science and technology cannot be permitted to be retarded by lack of attention to the human element. The ultimate

goal of industrial hygiene should be its acceptance as a necessary function in the design, construction and operation of an industrial plant.

Industrial hygiene has an excellent heritage built on a foundation of closely integrated cooperation of several disciplines with a common objective and specialized knowledge of the occupational environment, and its effects on man. Future pre-eminence in this field requires continuous and aggressive research, both fundamental and applied, to be prepared for the economic and social changes which are occurring at an ever-increasing pace. We are confronted with a dynamic challenge, for it is doubtful if any group so small in number has the opportunity to contribute so much to so many.



Dr. H. H. Schrenk, left, receiving the Cummings Memorial Award from Dr. Lester V. Cralley, President of the American Industrial Hygiene Association, at the banquet of the Association's Eighteenth Annual meeting in St. Louis, April 24.

# Can An Automatic Blood Cell Counter Be Modified for Use in Dust Counting?

ROBERT P. CHRISTMAN

ANDREW D. HOSEY, Senior Sanitary Engineer (R)  
Occupational Health Program, U.S. Public Health Service  
Department of Health, Education and Welfare, Cincinnati

INDUSTRIAL hygienists and other scientists in this country and abroad for many years have sought some reliable method to reduce the time-consuming and fatiguing task of optical dust counting and particle sizing. In addition, a need exists for a technique to reduce or eliminate the inherent human errors involved in the presently employed optical methods. If a rugged, versatile electronic instrument for dust quantification were available, more dust counts could be made in less time and the results would be more reliable.

During the past decade researchers have investigated the use of various electronic devices for automatically counting and sizing dust particles and blood cells. Much of the work done in England was reviewed at a conference on "The Physics of Particle Size Analysis"<sup>1</sup> arranged by the Institute of Physics and held at the University of Nottingham, April 1954. In this country, LaMer, *et al.*,<sup>2</sup> Guyton,<sup>3</sup> Gucker, *et al.*,<sup>4</sup> Sinclair,<sup>5</sup> Fisher, *et al.*,<sup>6</sup> and others developed instruments for the automatic determination of particulate concentration and size distribution. In 1953, an automatic blood counter\* was offered to the American market. Design of this instrument, based on the monograph of Lagercrantz,<sup>7</sup> was begun without knowledge of the English research referred to previously.<sup>1</sup> The resultant instrument, while somewhat similar to one devised by MacFarlane and co-workers,<sup>8,9</sup> differs from it in several important respects.

This report does not constitute an endorsement by the Public Health Service of the instrument described for use either as a blood cell or dust counter.

Mr. Christman is presently employed as an Experimental Physicist by Westinghouse Atomic Power, Pittsburgh, Pennsylvania.

\*Known as the JA-Co Blood Arithmometer, this instrument was designed by the Jarrell-Ash Company.

The purpose of this paper is to report on a six-month project, begun in November, 1955, to appraise the automatic blood cell counter for dust counting. It is hoped that the information will prove valuable to others interested in an automatic dust counting system.

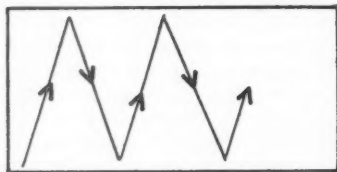
Most of the instruments to date are based primarily on the Mie<sup>10</sup> theory of light scattering. There are, however, many variations in the instruments which have been developed. Some are based on absorption of light while others utilize the principle of photoextinction. Guyton<sup>3</sup> developed an electrostatic method of particle analysis while others have been based on ultrasonic techniques. Some of the instruments used for dust and blood cell counting employ scanning methods. These may be electronic, where a field is scanned with a spot of light; or mechanical where an objective slide is mechanically moved between a stationary light source and a photomultiplier tube.

Mechanical methods of scanning may be subdivided further according to the optical system used—light or dark field illumination. In the former, dust particles intercepting the light beam reduce the light energy reaching a photomultiplier; on the other hand, in dark field illumination, dust particles reflecting the light beam yield pulses of light energy which are recorded by a photocell and amplified. The instrument described in this report operates on this latter principle.

## Description of Automatic Blood Cell Counter

FIG. 1 shows a functional block diagram of the apparatus. Darkfield illumination is provided in such a manner that the lower

20 microns of the counting cell are in focus. The counting cell is a custom made, optically flat, glass slide, about  $1\frac{1}{4}$  inches wide and three inches long. Each short side is built-up so that the cover plate, which is held tightly by two spring steel clips, allows a cell depth of 100 microns. This cell is placed on a movable platform or stage and is mechanically passed between the light source and objective to enable the scanning path to be a back and forth series of diagonal lines across the slide thus:



The light beam, after passing through the sample, is reflected at a right angle and is restricted by means of an aperture to an area  $150\mu$  by  $150\mu$ . Since the optical amplification is 20X, the effective area of the scan is  $7.5\mu$  by  $7.5\mu$ . With these slit dimensions the sample is scanned for a total length of approximately 1440 mm in 72 diagonal paths across the sample area. The scanning mechanism then reverses itself, increases the slit area to  $400$  by  $150\mu$  (or  $20\mu$  by  $7.5\mu$  at the sample) and sweeps a path similar to the original scan.

When the slide is observed from beyond the slit, light reflected from the particles appears as light streaks something like this:

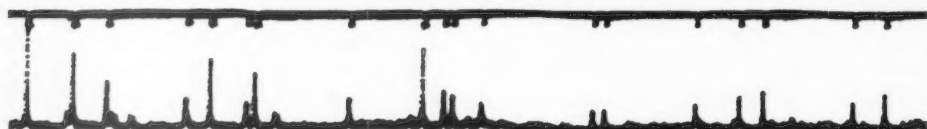


Forward scan, small  
slit width ( $7.5\mu$ )



Backward scan,  
slit width ( $20\mu$ )

These light paths then impinge upon the cathode of a photomultiplier tube where the light energy is converted to electrical pulses. If these are fed into an oscilloscope and photographed at a film speed of 3600 inches per minute, this is how they look:



The lower base line shows the output of the photomultiplier tube. The top trace is the output of the shaper circuit taken from the shaper output jack located at the rear of the instrument.

From the phototube the pulse is amplified, run through a pulse width discriminator circuit (an electronic gate opens if the pulse width is greater than 175 microseconds thus blocking or filtering out noise of considerable amplitude because of its narrow pulse width), and shaped into uniform size pulses which are conveniently counted by the scaler circuits.

The particle count obtained from the  $7.5\mu$  scanning width is subtracted from zero so that after the forward sweep is completed a negative count results. Immediately upon completion of the forward scan, relays reverse the scan and increase the scanning width to  $20\mu$ , and these counts are added to the forward count. Since the particles counted during the back sweep are greater than those counted during the forward sweep a net positive count results. This should be indicative of the center particles only, since the number of edge particles should be the same for both scans for a Poisson distribution of particles. With both scans completed, a net positive count results and pulses at the rate of 600 per second are electronically added to these counts until a total of 1,000 to 10,000 (adjustable) pulses are stored in the counter. During the time pulses are fed into the counter by the fixed frequency oscillator, a synchronous motor drives the indicating dial which stops on a scale indicating the number of blood cells (when used for blood) in millions of cells per cubic millimeter of blood. An exponential scale is primarily used to account for coincident losses which occur with random distribution of particles on the slide.

### Experimental Approach

IT WAS obvious that the dial read-out mechanism used in blood counting would have no value in dust counting, so it was decided

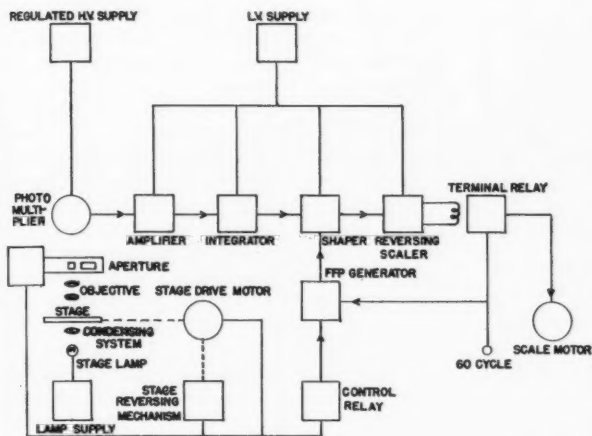


Fig. 1.

to attach a separate electronic scaler, taking the input to the scaler from the shaper jack on the instrument. By checking the pulse output from this point with a cathode ray oscilloscope, the pulses were found to be essentially square, of equal amplitude (40 volts) and from 0.2 to 1.0 milliseconds wide. The scaler's sensitivity was then adjusted to accept only pulses of 30 volts or greater. The forward and backward sweeps were timed and found to be approximately 36 seconds each. The scaler was then set to sample 30 seconds of each of these sweeps and the total volume sampled was calculated. Volume for the two scans was:

Forward scan = 0.880 mm<sup>3</sup>\*

Forward scan	= 2.35
Back scan	= 2.35*

Net (back - forward) = 1.47\*

\*Based on a 30 second sample

Various materials were used in these experiments. Master stock solutions and subsequent dilutions were counted optically to determine the particle concentration. Volumetric dilutions of the stock solution provided an additional check on particle concentrations.

At first it was decided to count the dust by the conventional technique with the Dunn cell. Several checks indicated that the concentration obtained in the Dunn cell and the cell of the instrument under study were comparable. Therefore subsequent optical checks were made entirely with the latter cell. This technique followed throughout the remainder of the experiment, pro-

vided information on the distribution of particles in the cell.

A satisfactory procedure of cleaning the cell after each run consisted of rinsing the cell with tap water, dipping it in a synthetic detergent solution, rinsing with distilled water and wiping dry with lens tissue. No further difficulties were experienced in obtaining clean slides. During the course of the experiment, hairline scratches gradually were made on the slides and these slides were discarded.

One of the first characteristics checked was the ability of the instrument to reproduce results on any one sample. A series of tests was made using various materials in several size ranges. Quartz in the size fraction of  $3\mu$  to  $4\mu$  was used in the first run. The quartz was suspended in distilled water to form a stock solution containing approximately 10,000 particles per cubic millimeter. This stock solution was diluted 1:2, 1:4, 1:8, 1:16, 1:32 and 1:50. Counts were made using the original stock solution and the above dilutions. Optical counts were made up to and including the 1:16 dilution. The other concentrations were established through volumetric calculations.

Ten successive counts on the 1:2 and 1:4 dilutions are shown in Table I.

Similar results were obtained on the other dilutions showing satisfactory reproducibility of results on the same sample.

TABLE I.

Dilution	1:2		1:4	
	Instrument Forward Scan	Count x 128 Reverse Scan	(scaling factor) Forward Scan	Reverse Scan
	38.0	72.3	15.75	44.2
	39.8	72.5	16.2	44.0
	39.5	72.8	16.0	44.0
	37.4	68.0	15.5	43.0
	36.5	68.9	16.0	42.5
	38.0	77.6	18.4	42.5
	36.0	76.4	19.6	42.75
	37.1	75.9	19.1	42.1
	37.0	72.0	18.3	42.0
	36.25	74.8	17.5	42.1
Mean	37.6	73.1	17.2	42.9
Standard deviation	1.3	3.1	1.5	.9

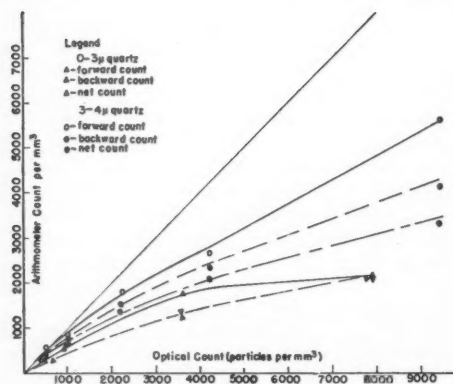


Fig. 2.

A series of similar tests was made on four dilutions of a 0 - 3 $\mu$  quartz suspension. Results of these tests using quartz are shown graphically in Fig. 2. The average of 15 counts, forward and backward at each dilution, was used to plot data for the 3 $\mu$  - 4 $\mu$  quartz and an average of five counts was used for the 0 - 3 $\mu$  material. The 45 degree line is the theoretical curve, assuming the optical count to be the absolute count, which would be obtained if the net counts were the same as the optical counts on an equal volume basis (particles per cubic millimeter). The forward count, as determined by the scaler, was divided by 0.88 (the volume scanned) to give the forward particle count in cubic millimeters. Backward counts were divided by 2.35. Net instrument counts were obtained by subtracting the total forward from total backward counts and dividing by 1.47 (net volume of scan). In the figures to follow, forward and backward counts in particles per cubic millimeter are plotted against optical counts. Net counts are shown for comparison in Fig. 2 only, but for all practical purposes, the forward counts more nearly approach the theoretical since the 7.5 $\mu$  scanning width permits the counting of sufficient whole particles as well as edge particles. The net counts are lower than either the forward or backward for 3 $\mu$  - 4 $\mu$  quartz but they are about the same as the backward counts on 0 - 3 $\mu$  quartz.

The response to 0 - 3 $\mu$  quartz is considerably below that of the 3 $\mu$  - 4 $\mu$  quartz. Since the instrument was designed for counting

blood cells which are about 8 $\mu$  in diameter, it is not at all surprising that apparently a great deal of the 0 - 3 $\mu$  material is not detected.

The lower count on this size material may be due to three factors: (1) coincident loss, (2) insufficient light produced by these particles, and (3) insensitivity of the detector. Coincident loss occurs when two or more particles are in the field at the same time. Obviously, the probability for coincident loss increases rapidly as the particle concentration is increased and the size decreased. The light energy scattered as these very small particles are scanned may not be sufficient to trigger the electronic counting circuit and hence individual particles are not detected. Perhaps two or more particles occurring simultaneously in the scanning area scatter sufficient light energy to be detected as one particle.

Four thousand particles per cubic millimeter correspond to a dust count of 20 mppcf based on a sample collected at 0.1 cfm for 20 minutes in 10 ml of liquid with a midget impinger. There is about a 50% difference between the instrument and optical count at this concentration of 3 $\mu$  - 4 $\mu$  quartz as shown by Fig. 2. At a concentration of about 10 mppcf the difference is approximately 20% and at lower concentrations the difference is 15% or less. The above comparisons are based on the forward count per cubic millimeter and the optical counts.

Response to particles having a median diameter of about 0.5 $\mu$  - 0.7 $\mu$  are shown in

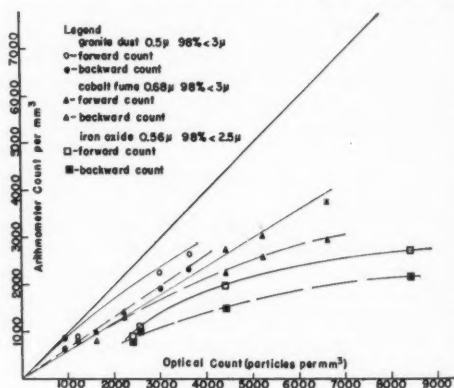


Fig. 3.



Fig. 3. The curves for granite dust and cobalt fume have essentially the same slope, but the cobalt fume curve lies below that for granite dust. This indicates a lower response to cobalt even though the median particle diameter is larger than that of the granite dust. The response to iron oxide is considerably below that for granite dust even though the median particle diameters are about equal. This indicates that the composition and refractive properties of the material affects the sensitivity of the instrument, perhaps to a greater extent than does particle size. This is shown also in the slope of the vanadium pentoxide curve in Fig. 4. While the mean particle diameter of the vanadium pentoxide is larger than the iron oxide, its slope is less, indicating a rather poor response to vanadium pentoxide. This is not too surprising since, particles of vanadium pentoxide under dark field illumination scatter rather small quantities of light. The instrument's response to such materials may be improved by increasing the sensitivity of the detector and by tuning the shaping circuit to accept pulses of lower amplitude.

The forward response to limestone dust (Fig. 4) closely approximates the theoretical curve up to about 2,000 particles per cubic millimeter. This is probably due to the larger ( $1.65\mu$ ) median particle size. However, the over-all instrument response is essentially the same as that for coal mine and granite dusts and cobalt fume since the slopes of these curves are about equal.

Forward counts of all the materials stud-

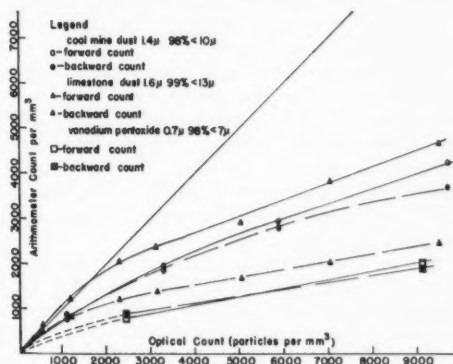


Fig. 4.

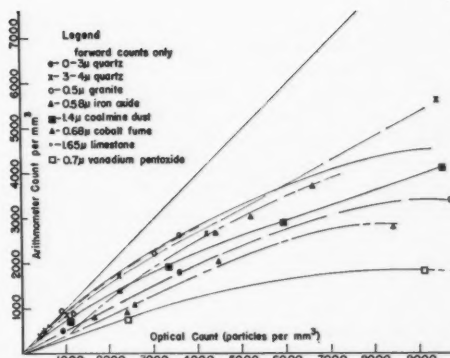


Fig. 5.

ied compared with their respective optical counts are shown in Fig. 5. All results are expressed in particles per cubic millimeter. This figure which summarizes the results of the several experiments indicates general trends to the various materials tested. Inspection of Fig. 5 shows that, of all the materials tested, the instrument response was poorest for vanadium pentoxide as indicated by the rather flat curve. Counts using iron oxide were somewhat higher and compare with those for the 0 -  $3\mu$  quartz.

Instrument counts with the other materials begin to decrease rather rapidly at an optical count of about 2500 particles per cubic millimeter. This is apparently due to an increase in coincident losses with increasing concentration. However, the maximum difference between optical and instrument counts is 40% for cobalt fume and coal mine dust, 28% for  $3\mu$  -  $4\mu$  quartz, and 20% for granite and limestone dusts at a concentration of 2500 particles per cubic millimeter. For some unknown reason, the cobalt fume curve does not approach zero nor does the curve for iron oxide in Fig. 3. One reason for this discrepancy may be that a certain minimum number of particles of these materials is necessary to trigger the counting circuit. Gross coincident counts during the reverse scan may account also for the low instrument response.

In the early stages of this study it was thought that there was little need for checking the automatic blood cell counter's performance on blood. However, the data obtained in the previous experiments indicated the instrument functioned primarily

as a proportional counter in dust counting. It was then decided to determine whether it was a primary counter when used for blood counting. The experiment was set up as follows: Blood was drawn from an individual, diluted one to 200 and counted by conventional techniques, using the Spencer Haemocytometer cell. A physician and medical technician made 10 counts each on the original dilution and determined the red blood cell count to be 5.06 million particles per cubic millimeter of blood. It was impossible to count the one to 200 dilution on the instrument directly, since the concentration at which it operates most effectively is at a dilution of one to 2,000. Consequently, an aliquot of the one to 200 dilution was further diluted to one to 2,000 and counted. On a series of four runs per slide, two slides produced the following dial readings: 4.62, 4.64, 4.62, 4.70, 5.23, 4.95, 4.93, 4.64 - an average of 4.79 million cells per cubic millimeter of blood.\* In addition to correlating the dial reading to optical counts, the narrow and broad slit pulses were recorded and net counts on a per volume basis were calculated. These values are also shown in Fig. 6 together with the net count (backward - forward total counts  $\div 1.47$ ). The dilution factors used were one to 2,000, one to 3,200, one to 4,000 and one to 8,000 of the original blood concentration. At least two slide preparations were made at these concentrations. Forward and backward counts were made with the instrument. An optical count was made using a 10X objective eyepiece graticule on all dilutions with the exception of the one to 8,000. This dilution yielded too few particles to be counted optically with any degree of accuracy. Fig. 6 shows that the net count agrees reasonably well (within 16%) with the optical count, up to a concentration of 2,500 red blood cells per cubic millimeter of solution. This equals five million particles per cubic millimeter based on the original blood concentration. For values of higher blood concentration, significant coincident counts occurred.

\*The manufacturer informed the authors that adjustment of the time delay circuit could have been made to give an instrument reading equal to the visual count. It is their practice to calibrate each instrument to agree with the visual counting standards of each hospital laboratory. Calibration of the instrument was not altered during any of the experiments reported in this paper.

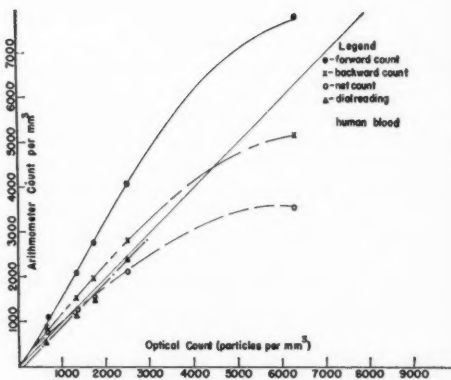


Fig. 6.

From this experiment it was concluded that the instrument probably performed as a primary counter for red blood cells, at least these experiments did not indicate otherwise. The fact that the automatic blood cell counter does operate as a primary counter greatly enhances the chances of it being modified for counting dust particles in the range of  $1\mu$  to  $5\mu$ .

### Summary

1. Results of these experiments on dusts at various concentrations indicate that the instrument studied is primarily a proportional counter.
2. Since it was designed for counting blood cells of approximately eight microns diameter and since most dust particles of hygienic significance range from about  $0.5\mu$  to  $5\mu$ , it seems reasonable to assume that its sensitivity is inadequate for dust counting.
3. It is also reasonable to assume that the dimensions of the aperture should be reduced to avoid excessive coincident losses.
4. If the automatic blood cell counter is modified for dust counting, provision should be made in the scanning mechanism or electronic circuitry so that the net count obtained would be indicative of a whole number of cubic millimeters of solution, preferably one.
5. Since coincident losses cannot be completely avoided, some method must be devised to correct for them. This becomes rather complicated in view of the variations in particle size of industrial dusts.
6. The instrument appears to perform



best at concentrations up to approximately 2,500 particles per cubic millimeter. However, if the aperture dimensions are reduced, slightly higher concentrations may be counted. For concentrations above 3,000 particles per cubic millimeter the coincident losses result in lower counts. Consequently, precautionary measures must be taken to insure that the actual concentration is sufficiently low to prevent this effect. In practice this may be accomplished by successive dilutions, recording only those net counts which result in a concentration below about 2,500 particles per cubic millimeter.

### Conclusion

NO INDUSTRIAL hygienist will deny the advantages to be gained from an automatic device for counting and sizing particulates. However, owing to the complexity of industrial dusts encountered in environmental studies, the authors do not know of any instrument that can completely and effectively replace the trained human evaluator. Many automatic instruments are in practical use today in conjunction with research projects. These may include monitoring dust concentrations in animal exposure chambers, recording various atmospheric pollutants and determining the concentration and size distribution of aerosols in checking the efficiency of various filter media.

Limited tests indicated that before the automatic blood cell counter can be used for dust counting, several modifications must be made:

1. Development of a photomultiplier tube with exceptional sensitivity and an extremely high signal to noise ratio.
2. Reduction of aperture and further study to determine the most effective slit size.
3. Correction for coincident losses and additional study to more precisely define these losses.

4. Selection of the volume of sample scanned as a whole number, preferably one, to simplify calculations of net counts.

### Acknowledgements

THE AUTHORS express their appreciations for the assistance given by R. E. Bales and H. E. Ayer for making many optical dust counts; N. A. Talvitie for furnishing size fractions of various dusts; Dr. Jacob Berghuis and V. B. Perone for preparing and counting blood samples; H. H. Jones for operating the oscilloscope camera and processing film; and to other staff members for guidance at various stages of the project and in the preparation of this report.

Appreciation is particularly expressed to the Jarrell-Ash Company for use of the Blood Arithmometer, technical information obtained during this project, and the constructive suggestions offered following a review of this report.

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## Industrial Hygiene Positions

THE Executive Secretary of the AMERICAN INDUSTRIAL HYGIENE ASSOCIATION maintains a list of positions in the field of industrial hygiene. Prospective employers and those seeking employment in industrial hygiene are encouraged to make use of this service. Inquiry should be directed to GEORGE CLAYTON, Executive Secretary, AIHA, 14125 Prevost, Detroit 27, Michigan.

# Field Studies of Atmospheric Diffusion and the Structure of Turbulence

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SINCE atmospheric pollutants are transported and dispersed by the wind, meteorologists have a self-evident interest in this branch of industrial hygiene. Although present knowledge suffices for satisfactory estimates of diffusion under certain conditions, the physical processes responsible for the dispersal are not well understood. Scarcity of experimental data is the principal reason for this lack of understanding. Diffusion equations in current use (Sutton, 1947a, 1947b; Calder, 1952; and others) are based in part on experiments made at Porton, England over a travel distance of 100 m in conditions of neutral stability (negligible vertical temperature gradient). Neutral stability is characteristically a transient state of short duration occurring between the usual daytime lapse (temperature decreasing with height) and the nighttime inversion (temperature increasing with height). The Porton results cannot easily be extrapolated to include the more frequently-encountered states of thermal stability and instability. The vertical gradient of mean wind speed is the principal meteorological factor employed in the above equations to predict diffusion. This indirect turbulence indicator is identified with the classical approach to atmospheric diffusion in which attention is focused on time-mean averages of meteorological quantities.

Research at the Round Hill Field Station has been guided by a different point of view that is gaining wide acceptance. It is felt

that improved understanding of the physics of diffusion requires empirical studies of the structure of atmospheric turbulence. The current research program has a two-fold objective: simultaneous field measurements of diffusion and meteorological parameters, including fluctuations in wind velocity as well as the vertical gradients of mean wind speed and air temperature; establishment of empirical relations between diffusion and meteorological factors. The purpose of this paper is to describe a series of experiments of this type carried out during the past two years, and to summarize the results thus far obtained.<sup>1</sup>

## Experimental Techniques

THE DIFFUSION experiments involved measurements of average concentration at selected points downwind from a continuous point source. The source utilized a 100-lb cylinder of sulfur dioxide immersed in a constant-temperature water bath. For source operation, the heat of vaporization required to transform the sulfur dioxide from a liquid to a gas was largely supplied by the water. The rate of gas emission ( $5$  to  $10$  g sec<sup>-1</sup>) could thus be maintained constant throughout the release period. The total amount of sulfur dioxide emitted during an experiment registered on the dials of a large gas meter. The gas was conducted through a 100-foot length of tubing to the release point which was at a height of 30 cm above ground level.

The sampling network comprised 183 stations spaced at intervals of three degrees along three semicircular arcs concentric to the release point; arc radii were 50, 100, and 200 m. Midget impingers mounted at a height of 2 m were used to determine average gas concentrations at each sampling

<sup>1</sup>Research sponsored by the Geophysics Research Directorate, Air Force Cambridge Research Center, under Contract No. AF 19(604)-1058.

An intensive study of diffusion on an expanded scale, using similar instrumentation and techniques, was conducted during the summer of 1956 under the sponsorship of the Air Force Cambridge Research Center (Project Prairie Grass).

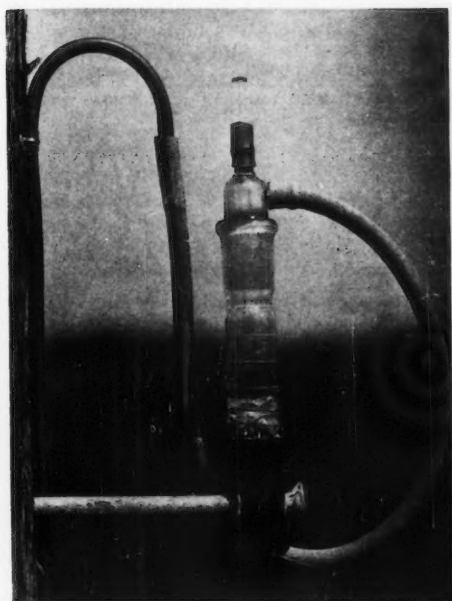


Fig. 1.

Field installation of midget impinger used to measure gas concentrations.

station. A typical field installation of a midget impinger is shown in Fig. 1. Air enters the impinger through the short section of capillary tubing shown at the top of the photograph, and is bubbled through 10 ml of a dilute (slightly acidified) hydrogen-peroxide solution. Sulfur dioxide present in the air sample reacts with the hydrogen peroxide to form sulfuric acid, thus increasing the electrical conductivity of the solution. Aspiration at the rate of  $1.5 \text{ l min}^{-1}$  was provided by vacuum pumps located at the center of each semicircular arc; the impinger is connected to the vacuum line through the flexible tubing shown at the center of the photograph. Prior to the start of an experiment, the source was turned on and the tracer permitted to traverse the entire sampling network. Aspiration of the impingers and operation of the meteorological instrumentation described below were then carried on for a 10-minute period. Average gas concentrations were determined in the laboratory by measuring the conductance of the aerated impinger solutions with a conductivity cell and a

Basic empirical relationships between the dispersal of airborne material and the structure of atmospheric turbulence are investigated by field experiments involving simultaneous measurements of diffusion and meteorological parameters. A tracer, sulfur-dioxide gas, is released for ten-minute periods from a continuous point source near ground level. Average gas concentrations are determined from changes in the electrical conductivity of absorbing solutions contained in midget impingers. Sampling stations are at a height of 2 m along three concentric semicircular arcs at travel distances of 50, 100, and 200 m from the source. Meteorological measurements include: vertical gradients of mean wind speed and air temperature from cup anemometers and ventilated thermocouples installed on a portable tower; fluctuations in wind speed, azimuth and elevation angle at a height of 2 m using fast-response bivanes equipped with heated-thermocouple anemometers. Analysis of experimental data shows that concentration profiles at the three travel distances are largely explained by the frequency distribution of azimuth wind direction. Under conditions of thermal instability (daytime), the reciprocal of the standard deviation of azimuth wind direction is an excellent predictor of peak concentration, integrated-crosswind concentration, and plume width. Prediction of these diffusion parameters under thermally stable conditions (nighttime) is more complicated; it appears that the combination of the inverse standard deviation of azimuth wind direction with either the stability ratio or Deacon's  $\beta$  will permit improved estimates of dispersal. The data show that changes in peak and integrated-crosswind concentration with increasing travel distance are not adequately explained by simple power laws with constant exponents.



Fig. 2.

View of meteorological instrumentation within the sulfur-dioxide sampling network.

Wheatstone bridge. This technique permits accurate determination of concentrations as low as 0.01 parts per million. Collection efficiency of the impingers was in excess of 95% for all experiments reported in this paper.

Meteorological instrumentation included: cup anemometers and ventilated thermocouples (installed at heights of 1.5, 3, 6, and 12 m on a portable tower) for determining vertical gradients of mean wind speed and air temperature; a cup anemometer and wind-direction vane (located at a height of 2 m near the gas-release point) to measure mean wind speed and variations in azimuth wind direction; four bivanes equipped with heated-thermocouple anemometers to measure fluctuations in wind speed, azimuth and elevation angle. Some of this instrumentation is shown in Fig. 2. Two bivanes, mounted on tripods, appear at the left and center of the photograph. The light vanes, which are free to move both vertically and in the plane of the horizon, are at a height of 2 m; these movements are transmitted to microtorque potentiometers located in the bases of the instruments. Heated-thermocouple anemometers are attached to the vertical shafts of the bivanes and are kept headed into the wind by the movement of the vanes in the azimuth plane. Chart recorders and auxiliary electrical apparatus are installed in the trailer shown in the background. The port-

TABLE I.  
LINEAR CORRELATIONS BETWEEN DIFFUSION AND  
METEOROLOGICAL PARAMETERS

Variates	Daytime (unstable)	Nighttime (stable)
$X_P$ , $1/\sigma_A$	0.93	0.72
$X_P$ , SR	0.60	0.49
$X_P$ , $\beta$	-0.71	-0.63
$X_{CIC}$ , $1/\sigma_A$	0.90	0.71
$X_{CIC}$ , SR	0.54	0.77
$X_{CIC}$ , $\beta$	-0.79	-0.52
$W$ , $1/\sigma_A$	-0.91	-0.52
$W$ , SR	-0.78	-0.43
$W$ , $\beta$	0.71	0.75

able tower used in determining the vertical gradients of mean wind speed and air temperature appears at the right of the illustration. A more detailed account of this instrumentation may be found elsewhere (Cramer, Gill, and Record, 1954).

#### Data Analysis and Discussion of Results

DATA from 29 experiments are available for study. Approximately half of the measurements were obtained during the daytime when the air near the ground was thermally unstable; the remainder of the data were obtained at night in the presence of temperature inversions. To facilitate comparisons, average gas concentrations for the 10-minute sampling periods have been reduced to standard conditions of source strength ( $1 \text{ g sec}^{-1}$ ) and mean wind speed ( $5 \text{ m sec}^{-1}$  at a height of 2 m). In addition, daytime concentrations along each arc have been smoothed by a weighted three-term moving average; nighttime concentrations are unsmoothed. The following characteristic features of the time-mean gas plume have been evaluated at the three travel distances:

Peak concentration  $X_P$  — the maximum observed concentration. Integrated-cross-wind concentration  $X_{CIC}$  — the product of the sum of all concentrations along a sampling arc and the linear separation distance between individual impingers. Plume width  $W$  — angular width of the plume defined by concentrations equal to, or exceeding, 10% of the peak concentration.

Empirical relations between the above diffusion parameters and three meteorological parameters are summarized in Table I. The standard deviation of azimuth wind direction  $\sigma_A$  was computed from the 10-minute chart records of azimuth fluctuations. The stability ratio SR, an index of thermal

stability, is given by the ratio of the mean temperature difference between two height levels (6 m and 1.5 m) and the square of the mean wind speed at an intermediate level (3 m). The parameter  $\beta$ , used by Deacon (1949) and others to predict diffusion, reflects the degree of curvature in the vertical profile of mean wind speed. For simplicity, the tabulated values are averages of the correlation coefficients at the three travel distances; the averaging technique is described by Fisher (1946, p. 204). The effective sample size is 24 for the daytime correlations, and 28 for the nighttime coefficients. Estimates of the percentage variation common to the variates may be obtained by squaring the correlations. The results indicate that, under conditions of thermal instability, the reciprocal of the standard deviation of azimuth wind direction is the most satisfactory predictor of all three diffusion parameters. Lowry (1951) found that the standard deviation of azimuth wind direction was a useful empirical index of ground-level concentrations associated with emission from an elevated source. The results for the nighttime experiments are not so clear-cut. For predictions of peak concentration,  $1/\sigma_A$  and  $\beta$  are superior to the stability ratio; in the case of integrated-crosswind concentration, the stability ratio and  $1/\sigma_A$  are superior to  $\beta$ ; the parameter  $\beta$  is the best predictor of plume width. The possibility of improving the prediction of nighttime diffusion parameters by combining meteorological factors is currently being investigated. Scatter diagrams showing the relation between concentration and the inverse standard deviation of azimuth wind direction are presented in Fig. 3; the solid lines were fitted to the data by the method of least squares.

Concentration profiles and the frequency

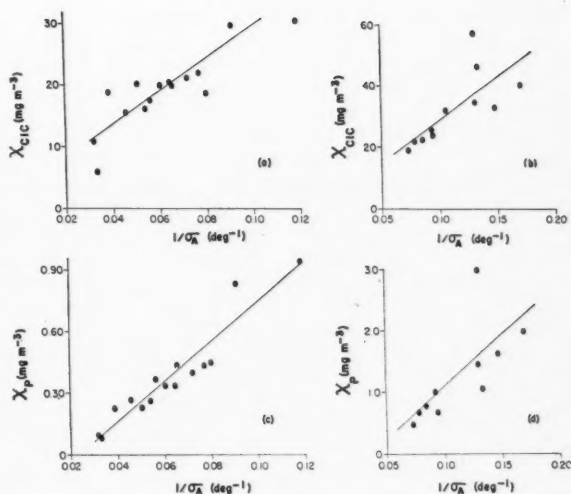


Fig. 3.

Scatter diagrams of peak and integrated-crosswind concentration at 100 m versus inverse standard deviation of azimuth wind direction. Daytime values are shown in sections (a), (c); nighttime values appear in sections (b), (d).

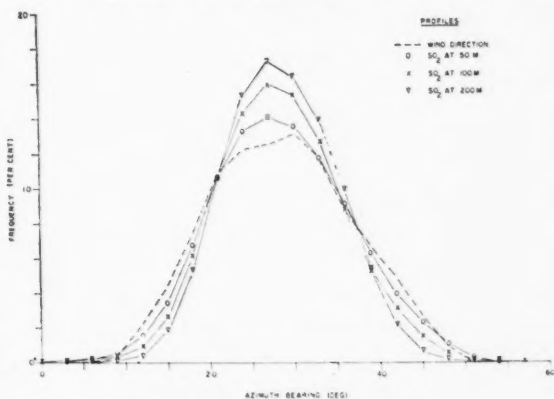


Fig. 4.

Concentration profiles and frequency distribution of azimuth wind direction for a daytime experiment.

distribution of azimuth wind direction for one of the daytime experiments are shown in Fig. 4. The profiles are obtained by expressing measured concentrations at individual sampling stations as percentages of the sum of all concentrations for a particular semicircular arc. While the data presented in the above figure have been



specially selected for illustrative purposes, the general features are characteristic of all the experiments. As might be anticipated, the agreement between the azimuth wind-direction data and the concentration profiles is best at 50 m. At greater travel distances, the angular plume width decreases, due to enhanced dilution at the edges, and the concentration profile tends to become more peaked. These results suggest that the time-mean plume is made up of elementary filaments that have traveled outward from the source in approximately straight lines. In other words, it appears that over short travel distances there is a scale of turbulence for which the Lagrangian correlation is approximately unity.

Changes in peak and integrated-crosswind concentration with travel distance  $X$  have been investigated by fitting data from individual experiments to power-law expressions of the general form

$$X_P, X_{CIC} \propto X^{-b}$$

where  $b$  is a constant. This has been done for two distance intervals: 50 to 100 m, and 100 to 200 m. Average values of the exponent for both daytime and nighttime experiments are presented in Table II. It is to be noted that, in all cases, the larger absolute values of  $b$  occur over the 100-200 m interval. Very few exceptions to this general behavior are noted in the data for individual experiments. It should be pointed out that the nighttime data may overestimate the increase with distance in the absolute value of the exponent. In the presence of light winds and strong temperature inversions, the plume axis remains close to the ground. At short travel distances, the maximum axial concentration may be below the height of the sampling network (2 m).

TABLE II.  
AVERAGE VALUES OF POWER-LAW EXPONENT  $b$   
FOR TWO INTERVALS OF TRAVEL DISTANCE

	Peak concentration		Integrated-crosswind concentration	
	(50-100 m)	(100-200 m)	(50-100 m)	(100-200 m)
Daytime	1.79	2.08	0.92	1.29
Nighttime	1.26	1.56	0.63	0.86

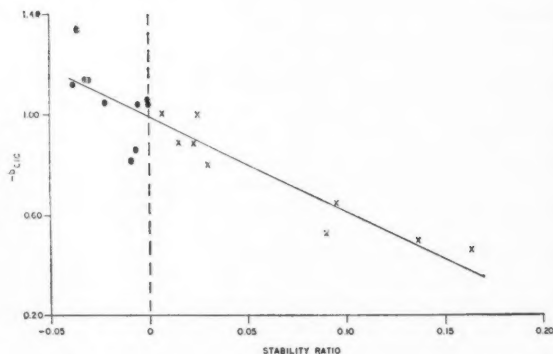


Fig. 5.

Power-law exponent  $b$  for integrated-crosswind concentration (50-200 m) versus the stability ratio. Daytime values are shown to the left of the dashed vertical line and nighttime values are at the right.

While this type of data has been excluded from the above computations so far as possible, some cases may have gone undetected. However, the evidence is fairly conclusive that changes with distance in both peak and integrated-crosswind concentration are not adequately explained by simple power laws with constant exponents.

The contribution of mechanical and thermal convection to dispersal is indicated by the values of  $b$  for integrated-crosswind concentration. For example, when  $b = 0$ , the spreading of the plume is entirely along a lateral or crosswind coordinate and the convective contribution is zero. When  $b > 0$ , a net flux of the tracer along the vertical coordinate is indicated. In Fig. 5, the exponent  $b$  for integrated-crosswind concentration has been plotted against the stability ratio. The dashed line ( $SR = 0$ ) represents neutral stability and serves to separate the daytime data (at the left) from the nighttime data (at the right). As might be anticipated, large positive values of the stability ratio are associated with small values of  $b$ ; this indicates the effectiveness of temperature inversions in suppressing the upward flux of gas contained within the plume. The solid line has been fitted to the data by the method of least squares; the linear correlation coefficient for the points shown in the figure is about  $-0.90$ .

### Conclusions

RESULTS of this preliminary analysis of the experimental data indicate the feasibility of establishing significant empirical relationships between diffusion and simple meteorological parameters. Although conclusive proof of the validity of the relations described above requires additional measurements, the following tentative conclusions are suggested. Under conditions of thermal instability, prediction of characteristic features of the time-mean plume (peak and integrated-crosswind concentration, plume width, etc.) over short travel distances appears to be a relatively simple matter.

In particular, the reciprocal of the standard deviation of azimuth wind direction explains approximately 80% of the observed variation in these quantities over a travel distance of 200 m. Prediction of diffusion in conditions of thermal stability is more complicated. However, it appears that improved estimates will result from a combination of the reciprocal of the standard deviation of azimuth wind direction

with either the stability ratio or the wind-profile parameter  $\beta$ . It also appears that changes in both peak and integrated-crosswind concentration with distance are more complicated than previously assumed. The results indicate that simple power-law expressions with constant exponents do not adequately represent these variations.

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## Anti-Smog Program

AN EXPANDED program to trace the sources and routes of smog and smoke in the New York-New Jersey area has been announced. Specialists from four Federal agencies will cooperate with local authorities in a scientific attack on problems of interstate air pollution. The program will use the personnel and facilities of four Federal agencies, the Army Chemical Corps, the Department of Agriculture, the Public Health Service and the Weather Bureau. Under general direction of the Interstate Sanitation Commission, scientists will attempt to determine the extent of smog in the area, its sources, and what effects, if any, it has on human health, plant life and economic development. Federal participation in the study will be coordinated by the U. S. Public Health Service. Part of the study will consist of an investigation by the Army Chemical Corps using a special technique to determine patterns of air currents and the extent to which they carry dust and smoke from one point to another. A second part of the study, to be carried out by Department of Agriculture personnel, will include evaluation of damage to plant life caused by air pollution. Public Health Service investigators will evaluate claims of damage or hazard to health resulting from air pollution while Weather Bureau installations will observe wind drift, sky conditions, and the effect of meteorological changes on pollution levels. FREDERICK S. MALETTE, consultant on air pollution problems, is directing the technical aspects of the Interstate Sanitation Commission program.



# Colorimetric Ultramicro Determination of Phenol in Air

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SEYMOUR HOCHHEISER, B.S., Chemist, and MORRIS B. JACOBS, Ph.D., Director  
Bureau of Laboratory, Department of Air Pollution Control  
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*The concentration of phenol in air in the range of two to 10 parts per 10 billion can be determined colorimetrically by means of the color produced when the phenol, after being trapped in an absorbing solution, is oxidized in the presence of p-aminodimethylaniline sulfate.*

IT HAS BEEN noted by the workers of the Battelle Institute<sup>1</sup> that phenol is one of the components of the exhaust from incineration of garbage and refuse. In our laboratory we have found micro quantities of phenol present in the air during days of high pollution. These concentrations are in the order of parts per 10 billion and consequently require an extremely sensitive method.

Gibbs<sup>2</sup> determined phenol colorimetrically by means of the reagents 2,6-dibromoquinonechloroimide and diazotized sulfanilic acid. Very likely diazotized sulfanilamide can be used in place of the diazotized sulfanilic acid. Hanke and Koessler<sup>3</sup> determined phenol by means of diazotized sulfanilic acid. Wetlaufer, Van Natta, and Quattlebaum<sup>4</sup> used acetic, nitric, and sulfuric acids. Phenol was estimated colorimetrically by Houghton and Pelley<sup>5</sup> by use of p-aminodimethylaniline. Jacobs<sup>6</sup> used this reagent for a qualitative test for phenol in air.

The latter reagent was found to be the most suitable for the quantitative determination of phenol in the order of parts per 10 billion in air. The basic amine reagent, however, was found to be very unstable and therefore was unsuitable for routine air pollution control work. In an attempt to

overcome this difficulty, the hydrochloride of the amine was prepared. This was found to be more stable than the amine itself. The acid sulfate was also prepared and this reagent proved to be quite stable. For this reason it was adopted as the reagent of choice. It is to be noted that this reagent also has been used for the determination of hydrogen sulfide.<sup>6,7</sup>

## Reagents

### 1. p-Aminodimethylaniline Sulfate Stock

**Solution:**<sup>7</sup> Mix 50 ml of concentrated sulfuric acid with 30 ml of water and cool. Add 20 grams of the amine, stirring until solution is complete. Make up to 100 ml with additional water. The amine sulfate may be purchased and used directly. p-Aminodimethylaniline Sulfate Test Solution. Dilute 5 ml of the stock solution to 100 ml with water.

2. Sodium Bicarbonate Solution - 0.5%: This is used as the absorbing solution.

3. Calcium Hypochlorite Solution - 0.1%.

4. Chloroform, Reagent Grade.

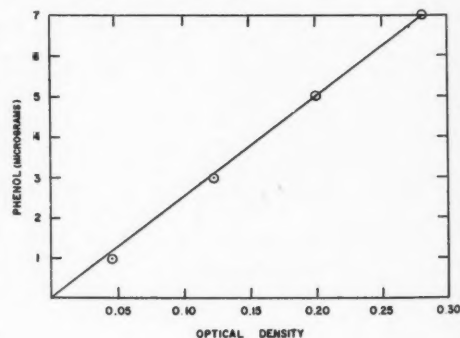


Fig. 1.  
Standard curve.

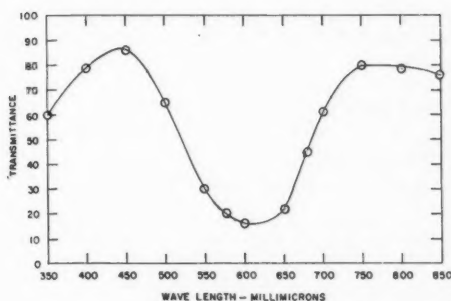


Fig. 2.  
Absorption curve.

### Preparation of Standard Curve

**STANDARD Phenol Solution**—Prepare a solution containing 100 micrograms of phenol per milliliter and standardize by the bromide-bromate method as detailed by Jacobs.<sup>6</sup> Prepare a solution containing one microgram per milliliter by dilution.

Add one, three, five, and seven micrograms of phenol to 45 ml of 0.5% sodium bicarbonate solution in a 125-ml separatory funnel. Proceed as detailed in the method. Determine the optical densities at 600 mμ using a blank as a reference. See Fig. 1. The final volume should be 10 ml. In our work, a Coleman Universal Spectrophotometer Model 14 was used. The maximum absorption was determined in the usual manner. See Fig. 2.

### Air Sampling

**THE ABSORPTION** efficiency of the sodium bicarbonate solution while sampling at a rate of one cubic foot per minute was determined in the following manner. One, three, five, and seven micrograms of phenol were dissolved separately in 5 ml of alcohol and were placed in large Greenburg-Smith impingers.<sup>6,8</sup> These were connected to fritted glass bubblers containing 45 ml of absorption solution. See Fig. 3. From 80 to 100% recovery was found after one hour of sampling.

### Method

**ASPIRATE** air at a rate of one cubic foot per minute through 45 ml of 0.5% sodium bicarbonate solution contained in a fritted bubbler. Transfer the solution to a 125-ml separatory funnel. Add four drops of the amine test reagent and then add 0.1% calci-

um hypochlorite solution dropwise until the pink color changes to blue or colorless. Allow to stand for five minutes. Extract with 10 ml of chloroform. Filter the chloroform layer through a pledget of cotton into a small test tube. Stopper the tube and allow to stand for 30 minutes. Determine the optical density at 600 mμ. Calculate the concentration of phenol from the standard curve.

### Results

**THE RESULTS** obtained by this method can be seen readily from Table I. The results obtained by use of this method in determining the amount of phenol in the New York City air on various days were of the same order of magnitude as Table I.

### Discussion

**AS MENTIONED**, the presence of phenol in air is indicative of days of high pollution. In our experience the concentration of phenol in the air of New York City is of the order of parts per 10 billion.

The most commonly used reagents for the determination of phenol are 2,6-dibromoquinonechloroimide and the Folin-Ciocalteu reagent.<sup>9</sup> Both of these reagents are quite sensitive and have been used for the determination of phenol in parts per million

TABLE I.  
ABSORPTION EFFICIENCY

Micrograms taken	Micrograms recovered
1	0.9, 0.80, 0.95
3	3.0, 2.95
5	5.0, 4.95
7	7.0, 7.0

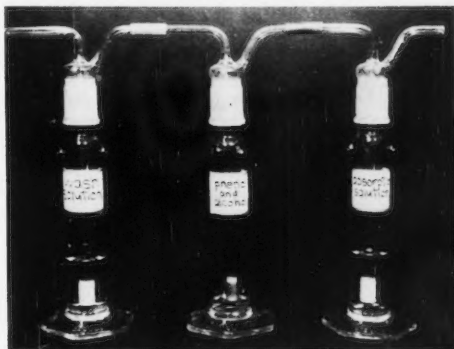


Fig. 3.  
Absorption efficiency train.

and per billion of water. There are several serious disadvantages to their use. The Folin-Ciocalteu reagent is difficult to prepare. The 2,6-dibromoquinonechloroimide reagent is not very stable. In addition, in the ultramicro concentrations in which we are interested at least four hours are required for full development of the color with the Gibbs' reagent. Indeed in the standard methods of water analysis a waiting period of overnight is specified. For our work a much more rapid method is required, thus *p*-aminodimethylaniline sulfate is preferred.

### Conclusion

**P**HENOLS in air in the order of parts per 10 billion can be determined by the use of the sensitive reagent *p*-aminodimethylaniline sulfate, by the use of 0.5% sodium

bicarbonate as the efficient trapping solution and a fritted glass bubbler as the trapping vessel.

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**S**EVERAL changes will be made at the end of 1957 which will affect subscriptions to the AIHA QUARTERLY. The journal will be published six times a year by the Williams and Wilkins Company of Baltimore. The name of the journal will be changed to the AMERICAN INDUSTRIAL HYGIENE ASSOCIATION JOURNAL. Members of AIHA will continue to receive the journal as one of the benefits of membership. Associate members may subscribe through the Secretary of the local section at a special rate. The annual subscription price in the United States starting January, 1958, will be \$7.50. The Canadian subscription will be \$7.75 and all other foreign subscriptions will be \$8.25. Subscriptions will be sold on a calendar year basis and will not be allowed to start in the middle of a volume. Orders for 1958 should be addressed to AIHA JOURNAL, % Williams and Wilkins Co., Mount Royal and Guilford Avenues, Baltimore 2, Maryland. Subscriptions for the remainder of 1957 should be addressed to AIHA QUARTERLY, 605 N. Michigan Ave., Chicago, Illinois. Two more issues will be published in 1957, in September and December. For those whose subscriptions end other than with the December issue, attention is directed to the need for partial orders. For the remainder of 1957, the AIHA QUARTERLY will be sold for \$1.00 per issue in the United States and \$1.25 per issue to all subscribers outside the U. S. Inquiries should be directed to AIHA QUARTERLY, 605 N. Michigan Ave., Chicago, Illinois.

# "Freon" Powered Portable Air Sampling Kit

R. C. CHARSHA and A. L. LINCH

Medical Division, Industrial Hygiene Laboratory

Chambers Works, E. I. du Pont de Nemours & Company, Inc.

Penns Grove, New Jersey

*An aspirator, designed for operation on compressed air for the driving force, has been adapted to constant pressure "Freon" operation. A limiting orifice installed ahead of the jet permits calibration based on time which eliminates the need for a metering instrument to determine sample volume. "Freon" is delivered from standard low-pressure "throw-away" refrigeration service cans, and standard midjet impingers are used.*

MOBILE air pollution surveys require analysis of "grab samples" which must either be taken to a laboratory for processing, or estimated in the field after passage through a solid, or liquid reagent designed to produce a distinct color change on contact with the expected contaminant. In collecting samples for laboratory analysis, several well standardized techniques are available:

1. The entire air sample is taken to the laboratory.
2. The contaminant is concentrated from a known volume of air by: (a) scrubbing through a liquid which either dissolves the soluble components, or acts as an arresting fluid for dust impingement, or (b) absorption on an activated, porous solid such as silica, or alumina gel.
3. Dust collection on a filter.
4. Precipitation of particulate matter by impingement, thermal deposition, or in an electrostatic field.

Concentration of the contaminants by absorption, filtration, or precipitation, as well as field direct colorimetric estimation requires movement of a known volume of air through the collection assembly. Electrically driven pumps adapted to some assem-

blies<sup>2</sup> cannot be employed where explosion hazards may be encountered, and the batteries, or long lengths of appliance cord needed for power add bulk and weight to portable units already burdened with collecting equipment. Availability of 110 volt a.c. current usually presents an obstacle as air sampling frequently is needed far from appliance outlets.

Hand operated mechanical pumps of three general types have offered the only practical alternative: (1) rotating vane<sup>3</sup>; (2) piston (usually a large volume glass syringe); (3) rubber, or Neoprene squeeze bulb such as commonly furnished with the solid granule supported indicator detectors for  $H_2S$ ,  $SO_2$ ,  $HCN$ , etc.<sup>5</sup>

These mechanical pumping devices reduce the analyst's efficiency by expenditure of nonproductive time and effort, require constant attention, and most are not suited to movement of relatively large air volumes required for accurate trace determinations. None of the types lends itself to the analysis of the atmosphere which a workman is actually inhaling while on his routine assignments.

Vacuum production by a high velocity gas, or liquid jet passing through a venturi is a well-recognized engineering principle widely applied in laboratories, and chemical manufacture.<sup>4</sup> Application in easily portable equipment has been delayed by a lack of self-contained supplies of gas, or liquid in light weight containers under sufficient pressure, and in quantities sufficient to draw a reasonable volume of air through the sampling system. Efforts were made to utilize liquid carbon dioxide,<sup>3</sup> and compressed air,<sup>1</sup> but the container weight, and high pressure hazards presented obstacles difficult to resolve.

A high efficiency "micro aspirator" which requires low gas flow rates to produce a usable vacuum became available during

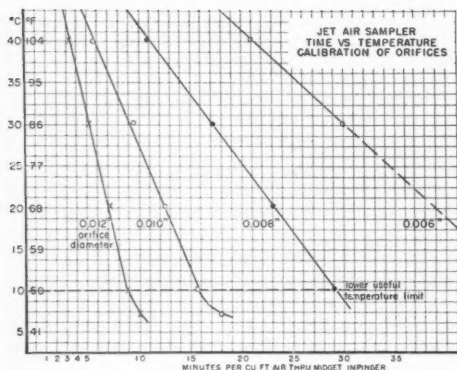


Fig. 1.

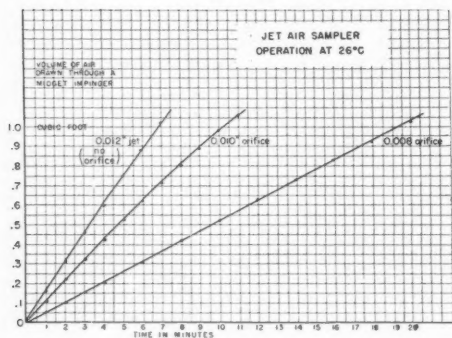


Fig. 2.

the past year.<sup>1</sup> Although originally designed to operate on compressed air, a modified venturi performs effectively on a "Freon" gas stream. Since a liquified gas offers the greatest space economy in transportation, selection of a low pressure "Freon" propellant in a light weight disposable container offered the most promising solution to the problems posed by a portable pressurized jet pump. Packaged "Freons" widely used in refrigeration equipment, and as a propellant for insecticides, paints, cleaners, and many other pressurized products are readily available in compact one-pound "throw away" containers. "Freon-12" is well suited for generation of comparatively large volumes of nonflammable, non-toxic vapor under pressure sufficient to activate the aspirator, but not of a magnitude that would present a rupture hazard under normal conditions.

The need for heavy bulky gas meters, rotometers and orifice meters, which require constant attention, or calibrated impingers used for manual pumping rate control is eliminated by introducing a limiting orifice between the gas supply and the venturi. Since the "Freon" pressure is a function of temperature (Fig. 3), the orifice calibration in terms of time required to draw a cubic foot of air through the sampling system must be corrected for temperature (Fig. 1). In the range 50° - 105° F the calibrations for six to 12 mils (thousandths of an inch) orifices are linear (Figs. 1 and 2). Below 50° F the calibration curve slope changes, but it is essentially a straight line to 20° F.

Fig. 4 shows an exploded view of an assembly which has performed consistently well under field sampling conditions. The discharge side of the needle valve supplied with the disposable can for recharging refrigeration units was rethreaded for 1/8-inch pipe. A 1/4-inch x 1/8-inch brass pipe bushing required to connect the valve to the aspirator was faced flat in a lathe to provide a seat to seal the polythene gasket against the orifice plate. Support for the orifice plate is provided by a spacer that holds the venturi nozzle in place against the flange inside of the aspirator body. The side tap on the venturi is fitted with an 1/8-inch pipe adapter for the rubber tubing connection to the midget impinger exhaust

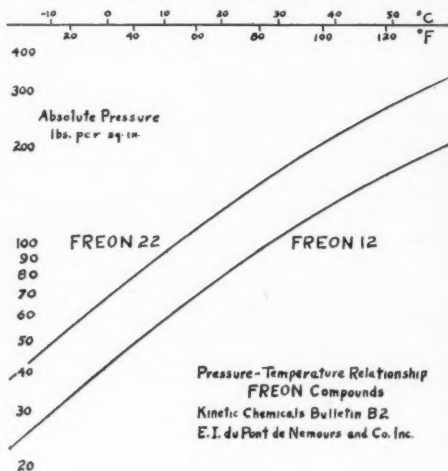


Fig. 3.





Fig. 4.

connection (Fig. 5). The seal between the needle valve port and the orifice plate must be gas tight as leakage at this point permits "Freon" loss without useful air aspiration and excessive chilling of the liquid "Freon" supply. Leakage at the tubing adapter will permit by-passing of the collecting scrubber, and give low results.

To operate, seat the valve snugly on the "Freon" container, assemble the aspirator on the valve port, open the valve wide (one to two full turns) to deliver full pressure against the orifice, and check for leaks. Soapy water, to which a few drops of glycerine has been added, applied with a small brush is an effective leak detector. Since the "Freon" pressure is dependent on temperature, this variable should be determined within  $\pm 1^\circ \text{F}$  to maintain volumetric error within  $\pm 2\%$  when sampling is started. A stainless-steel stem dial thermometer strapped in contact with the metal can is recommended. Best results are obtained when the charge temperature in the can is within a few degrees of the ambient air where sampling is to be carried out.

After connecting the sample collecting equipment to the vacuum (side port) outlet on the aspirator body with flexible tubing, or a filter adapter, the assembly is ready for use. Fig. 1 is a representative sample of a calibration chart employed to determine minutes required to draw one cubic foot of air through the midget impinger shown in Fig. 4 at temperatures

between  $50^\circ - 105^\circ \text{F}$  for each of four orifices. Fig. 2 is an isothermal plot of time versus air volume aspirated for the three larger orifices.

Although a midget impinger has been used exclusively by our Industrial Hygiene Laboratory, the choice of gas, vapor, mist or dust collecting apparatus is optional. The "Freon" vented from the aspirator does not under ordinary conditions dilute an air sample sufficiently to introduce significant error even when the impinger is closely coupled as in Fig. 4. However, in confined locations where there is no air circulation, samples collected near the floor may be diluted 10 - 15%. After operating 18 inches from the floor in an unventilated room containing approximately 500 cubic feet ( $6' \times 9' - 10'$  ceiling) for 10 minutes, air entering the impinger inlet contained 18% oxygen compared with 21% present initially. Approximately 1.25 cubic feet of "Freon" gas was released through a 10-mil orifice at  $26^\circ \text{C}$  during this period.

An adapter permits use of a "Millipore" micro-filter<sup>6</sup> directly on the side port of the aspirator body in place of the tubing adapter. Conversion to a Greenburg-Smith impinger, electrostatic precipitator, or absorption on porous solids is a simple operation. The choice of procedure for detecting the



Fig. 5.

TABLE I.  
PUMPING EFFICIENCY DETERMINED BY "FREON"  
CONSUMPTION RATE AND VACUUM PRODUCED

Parameter Measured	Orifice Size mil = 0.001 inch		
	8 mil.	10 mil.	12 mil.
Efficiency — Weight "F-12" per Cubic Foot of Air— Average (6 determina- tions) grams	52	55	59
Range (Temp. 70°-36°C) grams	±3	±3	±4
Vacuum — Static (open end manometer) mm Hg.			
10°C	19	27	31
26°C	21	40	96
40°C	25	70	124

expected contaminant whether a direct visual indicating color reaction for field analysis by comparison with a calibrated scale, or color standards, or collection for laboratory analysis must be selected by the analyst, as an evaluation of standard procedures is beyond the scope of the development of a portable, self-contained collecting device. The volumetric efficiency is surprisingly good (Table I). In the temperature range 45° - 97° F, the volume of expanded "F-12" gas consumed in aspirating one cubic foot of air lies in the range 0.375 to 0.425 cubic feet. One pound of "F-12" will "pump" seven to 10 cubic feet at one atmosphere.

Since the entire assembly ready for operation is compact, and weighs less than two pounds, the unit can be carried on a workman's back on a shoulder strap, or belt loop. By means of a flexible hose taped to his collar, continuous samples of the atmos-

phere that the subject is actually inhaling can be collected without interfering in any way with his routine job assignments. In this manner the question of representative sampling can be answered.

The "Jet Air Sampler" is available as a complete kit from the "Union Industrial Equipment Company," 175 South Main St., White Plains, New York. "Millipore" micro-filter adapters, midjet impingers, calibrated orifices, and supplies of "Freon-12" are also available.

### Summary

A COMPACT air sample collecting assembly weighing less than two pounds is powered by vaporization and expansion of non-toxic nonflammable "Freon" from a disposable container through a micro-aspirator. A limiting orifice in the "Freon" gas stream is employed in place of space consuming metering devices to determine sample volume from a time-temperature relation calibration chart. One pound of "Freon" will aspirate seven to 10 cubic feet of air through a midjet impinger, or filter.

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Department of Health, Education and Welfare  
Cincinnati, Ohio

**L**IGHT-SCATTERING techniques based on the electromagnetic theories of Rayleigh<sup>1</sup> and Mie<sup>2</sup> have been used to measure the size distribution as well as concentration of airborne dust particles since World War II. Although the theory and development of light-scattering instruments have been dealt with at length in the literature, no accurate yet practical method for interpreting the charts produced had been devised. We have developed such a method for assessing dust concentrations which, being empirical, automatically corrects for changes in the dust, in the electronic components, or in the contamination of the optical system which occur during normal use of the instrument.

### Discussion of the Theory

**T**HE INTENSITY of the light scattered from small particles ( $r < \lambda$ ) is dependent on the wavelength, the index of refraction and the sixth power of the particle radius as shown in the Rayleigh equation.<sup>3</sup>

$$I_\gamma = \frac{9\pi^2}{R^2} \left( \frac{m^2 - 1}{m^2 + 2} \right)^2 \frac{V^2}{\lambda^4} (1 + \cos^2\gamma)$$

where  $I_\gamma$  is the intensity of light scattered at the angle ( $\gamma$ ) measured between the direction of propagation of scattered light and the reversed direction of propagation of incident light.  $R$  is the distance from the particle to the point of observation and is large compared to the particle radius  $r$ . The letter  $m$  is the refractive index of the particle relative to air (complex for absorbing particles).  $V$  is the volume of the particle and  $\lambda$  the wavelength of the incident light.

For larger particles ( $r \approx \lambda$ ) the equation is given by Mie<sup>4</sup>

$$I_\gamma = \frac{\lambda^2}{4\pi^2 R^2} (i_1 + i_2)$$

where  $i_1$  and  $i_2$  are complex functions of  $\alpha$  ( $\alpha = \frac{2\pi r}{\lambda}$ ),  $m$ , and  $\alpha$  and are proportional to the intensities of the two plane polarized components in the scattered light.

In each of these cases the angular distribution of intensity varies according to some function of  $r/\lambda$  and while in the Rayleigh type of scattering, as much light is scattered in a backward direction as forward, as the particle radius increases the forward scattering becomes much greater; for  $r = \lambda$  may be 1000 or more times the backward scattering.<sup>5</sup> Thus on a theoretical basis the most sensitive light-scattering technique for assessing airborne dust concentrations is the measurement of light scattered in the forward direction or the small angle scattering.<sup>6</sup> This is accomplished in an instrument described by Sinclair<sup>7</sup> and now commercially available as the Sinclair-Phoenix Forward-Scattering Smoke Photometer<sup>8</sup> which utilizes essentially dark field illumination of the flowing stream of dust particles. Such an instrument is extremely sensitive to changes in the particle-size distribution of the aerosol being assayed which limits the applicability of the instrument to circumstances where this factor is unchanging. The monitoring of animal inhalation exposure chambers offers this ideal condition.

### Description of the Instrument

**I**N THE commercial instrument\* the optical system is so constructed that the only light which reaches the sensing element, in

\*The instrument tested was used as purchased with only slight modification by the author. This report does not imply an endorsement by the Public Health Service and may not be used, in full or in part, for promotional purposes.

this case a photomultiplier tube, is that scattered by the dust particles. The signal from the sensing element is passed through an electronic amplifier to a recorder which continuously plots the data. The range of the instrument covers five orders of magnitude of concentration using a logarithmic type of amplifier which decreases the voltage applied to the photomultiplier tube as the scattered light increases. This also safeguards the photomultiplier tube against burnout by an instantaneous flash of light from an accidentally introduced high dust concentration or an extremely large particle. The recorder is a self-balancing potentiometer which measures the voltage drop across a 5-ohm resistance. The range of the photometer can be decreased and its sensitivity (response to slight changes at low concentration levels) increased by replacing this 5-ohm resistor with a 10-ohm resistor. When this is done, a signal that previously gave half-scale deflection of the potentiometer now gives full-scale deflection. We equipped our instrument with 5- and 10-ohm resistances which can be chosen at will by throwing a toggle switch, thus providing maximal sensitivity for either high or low-level dust concentrations.

Since the sensitivity of the photomultiplier tube is highest at a wavelength of 4500 Å the color of the particles as well as the color temperature of the light source will affect the reading obtained with the instrument. The electronic components of the instrument are subject to changes with age. In spite of all precautions the optical components become increasingly contaminated with use and between periodic cleanings the stray or background light in the "dark field" causes the sensitivity to change considerably. Even the tungsten evaporated from the filament of the light source and deposited on the inside of the glass light bulb causes a reduction in lumens and consequent change in meter readings. Table I shows a range of dust counts associated with a single photometer reading during an operating period of approximately one month. It is seen that, although the average deviation from the mean was less than 30%, the actual change from 3.9 to 8.6 million particles per cubic foot amounted to 220%. It is thus apparent that the accurate interpretation of the strip-chart record produced by the in-

TABLE I.

The variation in dust counts giving a constant photometer reading is shown. The five samples were taken at intervals over a period of approximately one month.

Photometer Reading in millivolts	Av. of Duplicate Dust Counts mpcf.
1.4	3.9
1.4	4.7
1.6	4.7
1.6	7.3
1.5	8.6
1.5	5.9
Av. Dev.	1.7
% Dev.	28.8

strument cannot be reduced to a simple matter of reading a fixed linear scale.

### Calibration

THE INSTRUMENT can be calibrated most easily against a series of filters of known density. With no dust particles in the light path the amplifier is adjusted to give a scale reading of zero. With the dark field stop removed and the entire light output of the

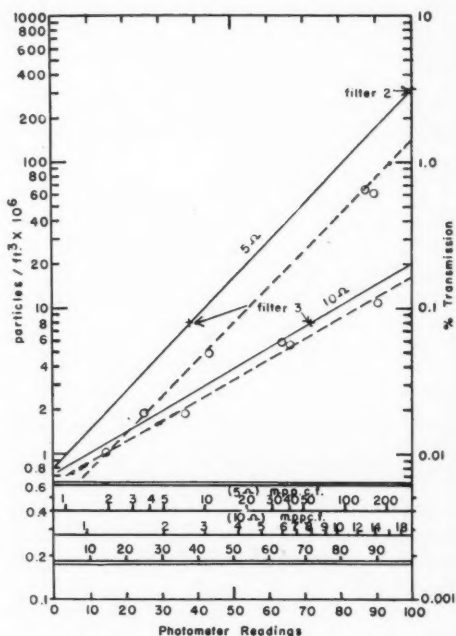


Fig. 1.

Typical calibration curves. Solid lines have been established by filters. Circles represent dust samples taken with the midget impinger and counted by the standard microscopic technique.

source allowed to strike the photomultiplier tube, the range adjustment is made to give full scale deflection. Neutral filters of known densities are then, in effect, substituted for the dark field stop and the meter readings between zero and full deflection are plotted on semilogarithmic paper against the filter values expressed as percent transmission. The filters used with our instrument have values of 3.25, 0.081, 0.0067% transmission. Fig. 1 is a typical plot of these data. The curve should approximate a straight line. Some log-amplifier circuits have trimmer adjustments in the circuit so that the response of the amplifier can be made truly logarithmic. The curve does not go through the origin due to the slight dark current in the phototube. A decrease in recorder deflection when one of the intermediate filters is in place can be taken as an index of reduced sensitivity or increased stray light in the optical system due to excessive contamination.

If a series of known dust concentrations is sampled with the instrument and the meter readings are plotted against concentration on the same semilogarithmic paper (dashed lines Fig. 1) the slope of the line produced should agree with that of the filter calibration curve if the amount of light scattered is proportional to the dust concentration. Sinclair<sup>9</sup> showed this is true as long as the dust concentration is sufficiently low and secondary scattering does not occur among the particles. In the commercial cell sufficient dust to cause secondary scattering would require a concentration of several billion particles per cubic foot.

Having established that the curve for the dust in question has the proper slope and parallels the filter curve, we can use the latter to produce the scale shown at the bottom of Fig. 1. This scale, while not truly logarithmic, is exponential and characteristic of the amplifier system used. It shows accurately the spreading out of the readings in the lower concentration ranges and the compression in the higher ranges. This scale was copied on a piece of clear lucite and mounted over the chart in the recorder in a manner permitting it to slide back and forth. Moving the scale sideways corresponds to raising or lowering the calibration curve while keeping the slope constant.

A series of samples taken at two-hour in-

TABLE II.

Variation of dust counts corresponding to a constant photometer reading during one day. The four samples were taken at approximately two hour intervals over a six-hour period.

Photometer Reading (millivolts)	Duplicate Dust Counts (mppcf.)	Av. of Dup. Dust Counts (mppcf.)
1.5	5.2 4.7	5.0
1.6	5.7 4.7	5.2
1.7	4.7 5.2	5.2
1.7	6.0 4.5	5.2
Av.	1.6	5.1
Av. Dev.	0.75	.4
% Dev.	4.7	8.6
		1.5

tervals over a six-hour period of constant photometer readings is shown in Table II. It is seen that the response to an unvarying dust concentration has not changed significantly over this period. The middle column which reports individual dust counts, shows that the deviation in the dust counting technique is greater than the deviation of the photometer readings and the instrumental variation is well within the limits of error of this method. Thus the use of a single sample each day to standardize the instrument is not unreasonable. In practice the photometer is adjusted for zero and 100% light transmission and allowed to sample continuously for the desired period. At some time during this period one sample is taken and the time and duration of the sample is marked on the strip chart. This sample is counted in duplicate and serves as the internal calibration for that six-hour period. At the end of the period the photometer readings for zero and 100% light transmissions are rechecked for assurance that the response of the instrument has not changed radically in six hours. The sliding scale is moved so that the scale value of the sample concentration coincides with the average meter value at the time the sample was taken. This then automatically corrects the instrument for drift or any of the other variables mentioned above within the accuracy of the sampling technique used. As the strip chart record passes under the scale the highest and lowest values can be read directly and a visual estimate of the average concentration for the entire period can be made.

The practical possibility and theoretical justification of super-imposing the filter calibration curve on the sampling calibration curve greatly increases the confidence in the calibration and the response of the instrument. Although the use of known density filters as standards is a natural choice for this particular instrument, the same sliding-scale technique would be equally applicable to any detector-amplifier-recorder combination where the response of the instrument to some stimulus, electronic or other, can be shown to agree with its response to the measured quantity.

### Experimental Results

TABLE III gives data obtained during a typical four-week period of chamber testing at three concentration levels. The dust being tested was silica dispersed by the Wright Dust Feed apparatus.<sup>11</sup> A series of particle-size measurements made by electron microscopy<sup>12</sup> during the course of the experiment showed it to have a mean particle size of  $0.61 \mu (\pm 0.05 \mu)$  and a standard

geometric deviation of  $2.9 (\pm 0.1)$ . No significant difference was noted between samples taken of the same concentration level on different days or between samples of the three levels tested. The two- and five-million particle per cubic foot concentrations were maintained for six hours daily five days a week. The same chamber of approximately 175 cubic feet capacity, was used for the 2- and 5-mppcf concentrations, one being run during the day and the other during an evening shift. The 50-mppcf level was maintained for one hour a day three days a week in a smaller chamber of approximately 25 cubic feet. All of these levels were monitored on one single-pen strip-chart recorder using the same photometer. The single daily sample was taken with the midjet impinger and the dust counted, using the Williams technique<sup>10,13</sup> with the optical microscope (10x objective and 20x eyepiece) and the hemocytometer cell. The mean photometer reading for the day was estimated from the recorder chart using the sliding scale described above and positioned according to

TABLE III.

Data obtained during a typical four-week period of a dust chamber concentration test at three levels. Dust concentrations are in millions of particles per cubic foot of air.

Date '56	2 mppcf			5 mppcf			50 mppcf		
	Daily Impinger Sample (mppcf.)	Photo-meter Mean (mppcf.)	Photo-meter Range (mppcf.)	Daily Impinger Sample (mppcf.)	Photo-meter Mean (mppcf.)	Photo-meter Range (mppcf.)	Daily Impinger Sample (mppcf.)	Photo-meter Mean (mppcf.)	Photo-meter Range (mppcf.)
4-30	2.0	2.2	1.7-2.6	5.8	6.0	5.0-7.0			
5-1	2.4	2.5	2.0-3.2	4.6	5.0	4.0-6.5	56	56	50-70
5-2	2.3	2.6	2.0-3.2	6.3	6.1	5.8-7.0			
5-3	1.9	2.6	1.8-4.0	4.1	4.7	4.0-6.0	42	40	20-48
5-4	2.4	2.4	2.0-3.0	5.2	5.5	4.5-6.5	54	55	50-90
5-7	2.0	2.5	1.8-3.2	5.4	5.3	4.5-6.5			
5-8	2.0	2.3	1.8-3.9	5.0	5.1	4.5-6.0	49	60	40-90
5-9	2.0	2.0	1.6-2.3	5.8*	7.0	5.0-10.0			
5-10	2.4	2.4	2.0-3.2	3.5†	3.7	3.0-5.0	57	92	35-55
5-11	2.6	2.7	2.0-3.5	4.3	4.8	4.0-5.8	54	50	30-65
5-14	2.9	2.3	1.7-2.6	4.3	4.5	3.5-5.5			
5-15	3.0	1.8	1.5-2.5	4.3	4.8	3.8-6.0	82	70	40-90
5-16	1.4	2.0	1.9-3.0	3.7	4.8	3.5-5.0			
5-17	2.1	2.2	1.5-2.5	4.6	4.7	3.5-5.0	59	50	40-60
5-18	2.3	3.0	2.2-4.0	4.7	4.3	3.8-5.2	69	60	40-80
5-21	2.7	2.6	2.3-3.2	4.3	4.0	3.5-5.0			
5-22	1.8	2.4	1.6-3.0	4.8	5.5	4.5-6.5	114	85	50-110
5-23	3.6	3.5	3.2-4.5	6.5	5.5	4.5-7.0			
5-24	1.7	2.2	1.5-3.0	4.8	5.0	4.0-6.5	91	70	50-90
5-25	2.8	3.0	2.0-4.0	6.3	6.1	4.5-8.0	39	70	30-95
Mean	2.3	2.5		4.9	5.1		64	59	
Deviation	.4	.3		.7	.6		17.7	6.1	
% Deviation	17.4	12.0		14.3	11.7		27.7	10.3	
Mean daily range			1.9-3.2			4.2-6.3			40-79

\* † See text.

the daily sample result. The photometer reading in millions of particles per cubic foot is therefore dependent on the daily sample. The high and low photometer readings for the day are listed in the column headed "Photometer Range." No equivalent of this information is possible except by using a continuously recording instrument. The average high and low concentrations have been calculated and listed at the foot of the table as the "mean daily range." The mean, deviation and percent deviation for the 20 daily values have also been calculated and listed under the appropriate columns at the bottom of the table. It will be seen that for the two lower concentrations the values are in fairly good agreement, although the use of the daily mean photometer readings results in a lower percent deviation than when the single daily samples are averaged. At the high concentration, however, the number of samples has been reduced from 20 to 12 and the difference between the continuously recorded values and the spot samples is considerable. Since the percent deviation of the photometer readings agrees closely with both of the lower concentrations, it may be assumed that this is a more accurate appraisal of the true concentration.

Fig. 2 shows the record produced on May 9th (Table I\*) for the 5-mppcf level which is a typical six-hour period. The chart reader shown was constructed to facilitate reviewing of the entire strip-chart roll which represents several months of operation. The dotted lines are drawn through the highest (10-mppcf) and lowest (5-mppcf) concentrations recorded and the dashed center line represents the visually estimated average concentration for the period (7 mppcf). The average photometer reading during the 20-minute impinger sampling period is marked and the sliding scale adjusted so that this line corresponds to 5.8, the dust count from the impinger sample, on the middle (10-ohm) scale. The high, low, and estimated average concentrations can now be read directly from this scale.

It is seen that the single impinger sample for the period (5.9 mppcf) does not agree with the average concentration recorded by the photometer (7 mppcf). On the basis of the impinger sample alone no adjustment

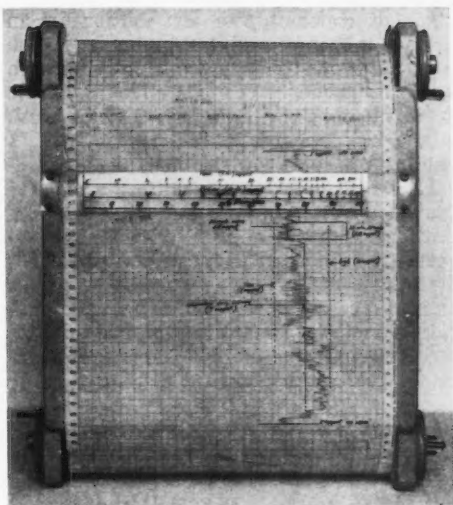


Fig. 2.

Chart produced during a typical six-hour operating period. The beginning and end of the period are marked as well as the duration and average photometer reading for the standard sampling period. The sliding scale has been adjusted so that 5.8 on the 10-ohm scale corresponds to the average during the impinger sampling period. The impinger sample, counted by standard techniques, was found to be 5.8 mppcf.

would be made to the chamber to reduce the dust concentration and presumably the following day would show the same high average concentration. However, on the basis of the photometer record the chamber airflow was adjusted to decrease the dust concentration. The correction was too great, to be sure, but the desired value was properly bracketed and the average concentration the following day (Table I†) of 3.7 mppcf shows the result of this correction. This type of precise control could not be exercised without the continuous record and direct reading scale of the photometer.

### Summary

THE EQUATIONS which describe the angular distribution of the intensity of light scattered by spherical transparent particles show that any instrument based on this theory which is used to measure dust concentrations will be extremely sensitive to changes in the size distribution of the dust. Monitoring the controlled dust concentra-



tions of constant size distribution in an animal inhalation exposure chamber is an ideal situation for the application of such an instrument. A commercially available forward light-scattering photometer with slight modifications is described here. A calibration curve of the instrument readings against known transmissions of neutral density filters was used to produce a scale recording the dust concentration directly in millions of particles per cubic foot. Data collected over a one-month period of typical operation show the precision obtained and the advantages of such an instrument over the more common grab sampling techniques.

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## Noise Reduction Program

THE Massachusetts Institute of Technology will present a Special Summer Program in Noise Reduction. The program will be separated into two one-week units. The first unit "Fundamentals of Noise Reduction" will be held August 12 to August 16 and the second unit, "New Advances in Noise Reduction" is scheduled for August 19 to August 23. Tuition for each unit is \$150.00. For application forms and further information, inquiry should be directed to the Office of the Summer Session, Massachusetts Institute of Technology, Cambridge 39, Massachusetts.

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# Determining Fluoride Air Concentrations

## —BY EXPOSING LIMED FILTER PAPER

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OVER 30 years ago British air pollution investigators began to study the atmospheric concentrations of sulfur dioxide by exposing a dry lead peroxide surface to the air and then analyzing the surface material for the sulfur materials which had collected there. Not much use has been made of this dry collection technique or static sampler in the United States although recently there has been some work on the determination of atmospheric fluorides using dry materials. This has been reported by Miller and his co-workers<sup>1</sup> at Washington State College in 1953, by Mavrodineau<sup>2</sup> of Boyce Thompson Institute in 1954, and by MacIntire, *et al.*,<sup>3</sup> in Tennessee in 1956. Techniques of this type offer obvious advantages from a cost standpoint, particularly when coverage of a large area is desired and short time resolution is not necessary.

The bases of the exposure method are the assumptions that gaseous fluorides will react with the material, thus becoming fixed to it, and that this reaction will take place at a constant rate so that comparisons can be made between material exposed to different fluoride concentrations. The main difficulty in the technique is in this latter assumption because, rather than responding to concentration values, as a sampler with constant air flow does, the exposed material responds to the total amount of fluoride brought in contact with it, and thus responds both to the fluoride concentration of the air and to the flow of air past the filter paper. It is sensitive to the air flow because it is only through the movement of the air that the fluoride is brought in contact with the material. If the air flow is doubled, roughly twice as much fluoride can be brought in contact, depending upon flow characteristics, even though the concentration is not changed. The deposition of particulate fluorides on the exposed material

depends upon the size of the particles as well as on all of the conditions of exposure, and would be extremely difficult to evaluate.

Miller reported on comparisons between the fluoride content of vegetation and the fluoride pickup of discs of filter paper which had been saturated with low-fluoride lime. Mavrodineau used paper treated with an indicator solution which gave an indication of concentration through changes in color. MacIntire exposed both limed filter paper and Spanish moss. While Spanish moss is actually a plant, it can generally be handled like an inert material and thus should probably be classed with filter papers as a static sampler. No data have been published which have related the various static sampling techniques to total atmospheric fluoride concentrations as indicated by conventional air sampling techniques.

### Methods

DURING a recent Stanford Research Institute air sampling program in an area where atmospheric concentrations of fluoride existed, it was possible to carry out some experiments with the filter-paper technique and to compare it to fluoride air sampling using water-filled scrubbers. Filter papers were exposed for various periods of time at locations where regular air samples were also being taken. In this way, the correspondence of the filter-paper samples to the existing atmospheric fluoride situation could be determined directly. The test exposures were carried out by hanging the filter papers\* in the open air rather than inside any covering. It was felt that the covering would add an additional, unassessable variable to an already complex situation. No rain occurred during the tests.

\*Whatman No. 1, 12.5 cm.

The papers were lime-treated by being soaked in a saturated solution of low-fluoride lime and then oven-dried. Analyses of the filter paper for fluoride were carried out using a modified ion-exchange technique.<sup>4</sup> The paper was slurried in distilled water, made slightly acid with hydrochloric acid, and the liquid was decanted into an ion-exchange column. The paper residue was washed with several changes of distilled water to assure good removal of the fluoride. The fluoride content of unexposed limed filter papers such as those used in these tests was one microgram of fluoride. No corrections were made for this relatively small blank content.

### Experiments

THE AREA used for the study contained a large industrial fluoride source. In addition, three greenhouses were available which were similar except for the fluoride concentrations which existed inside. Greenhouse No. 1 used outside air direct and had the highest fluoride concentration. Greenhouse No. 2 used outside air which had been passed through an untreated bag filter and had an intermediate concentration. Greenhouse No. 3, which used air that had passed through a bag filter in which the bags were coated with lime, had a very low concentration. Air flow through the greenhouses was about 3 mph. Plantings within the houses were approximately equal. Scrubber-type air-sampling units were used to measure actual air concentrations. With this arrangement it was possible to determine (1) how all other factors being reasonably constant, the fluoride accumulation in the filter paper varied with variations in the atmospheric concentration of fluoride; (2) how filter-paper sorption varied with variations in exposure conditions but with equal air concentrations of fluoride; and (3) by using sampling stations in the countryside surrounding the source, the variations in filter paper pickup under field exposure conditions were determined.

The variability of filter-paper fluoride sorption due to variations in exposure conditions but with equal concentrations of fluoride was examined by exposing the limed filter papers outside and inside Greenhouse No. 1. In this situation the filter papers inside the greenhouse were exposed

to a constant air flow of about 3 mph through the greenhouse, while those outside were exposed to the normal wind averaging about 8 mph at the site. Previous air sampling had already shown that air inside the greenhouse had a fluoride concentration comparable to that outside. Thus, the principal conditions which varied between the two samples, outside and inside, were air flow, temperature, and humidity. Two tests were run inside and outside the greenhouse. The filter papers outside the greenhouse collected 5.4 times as much fluoride during an 11-day test and 4.4 times as much during a two-day test as the papers hung inside the greenhouse. The individual test data are shown in Table I.

Even though the variations in conditions inside the greenhouse would be expected to be at a minimum, variations of the order of 60% occurred between these two tests. Thus, there were sufficient differences between the two test periods to influence markedly the rate of fluoride pickup by the filter papers, whether the papers were inside or outside the greenhouse. During Test 1, the papers outside the greenhouse picked up fluoride at a rate of 43 micro-

TABLE I.  
VARIABLE EXPOSURES TO EQUAL CONCENTRATIONS OF FLUORIDE

Filter Paper No.	Test 1	
	Outside Greenhouse	Inside Greenhouse
1	870 Micrograms F	140 Micrograms F
2	880	150
3	1000	180
4	1200	200
5		190
6		210
7		210
Average	988	183
Average air concentration for period = 2.11 ppb F		
Exposure = 11 days		
Filter Paper No.	Test 2	
	Outside Greenhouse	Inside Greenhouse
1	127 Micrograms F	23.5 Micrograms F
2	79	23.5
3	86.5	23.5
4	112	28.5
5	118	27
6	132	28.5
7	148	28.5
8	140	32
9	142	33
10	146	33
Average	123	28.1
Average air concentration for period = 2.72 ppb F		
Exposure = two days		

TABLE II.  
TESTS WITHIN SEVERAL GREENHOUSES WITH VARYING  
CONCENTRATIONS OF F

Test 3			
Filter Paper No.	Greenhouse No. 1	Greenhouse No. 2	Greenhouse No. 3
1	165 Micrograms F	17 Micrograms F	19.5 Micrograms F
2	93	13.5	17
Average	129	15	18
Average Conc. F (ppb)	1.62	0.14	0.07
Micrograms /day/ppb F	5	6	15
Exposure = 17 days			
Test 4			
Filter Paper No.	Greenhouse No. 1	Greenhouse No. 2	Greenhouse No. 3
1	215 Micrograms F	37 Micrograms F	4 Micrograms F
2	207	18.5	6
3	232	15	
Average	218	24	5
Average Conc. F (ppb)	2.31	0.18	0.11
Micrograms /day/ppb F	7	10	4
Exposure = 13 days			
Test 5			
Filter Paper No.	Greenhouse No. 1	Greenhouse No. 2	Greenhouse No. 3
1	302 Micrograms F	26 Micrograms F	10 Micrograms F
2	306	33	14
3	275	35.5	
Average	294	31.5	12
Average Conc. F (ppb)	1.97	0.16	0.10
Micrograms /day/ppb F	5	7	4
Exposure = 30 days			

grams per day per ppb F in the air and during Test 2 at a rate of 23 micrograms per day per ppb F. Inside the greenhouse the papers picked up fluoride at rates of eight and five micrograms per day per ppb F in the air during Tests 1 and 2, respectively.

Another group of tests to determine response to varying fluoride concentrations was carried out using the three greenhouses. Three tests were carried out in this part of the study and are tabulated in Table II. Air concentration values were around 2 ppb in Greenhouse No. 1, 0.16 ppb in No. 2, and 0.10 ppb in Greenhouse No. 3. In these tests the micrograms per day per ppb F varied from a high of 15 to a low of four, with an average of 6.9. The standard deviation, *s*, of these data is 3.2, which gives 95% confidence limits of 0.5 and 13.3. This spread, 93% of the mean, seems to prevent the use of the filter papers for quantitative results, although qualitative results could probably be obtained when large concentration differences existed, such

as those shown between Greenhouse No. 1 and either No. 2 or No. 3.

For the field tests, filter papers were exposed for seven days at a number of air sampling stations in the surrounding area. The locations selected were reasonably uniform and probably generally representative of the various local areas. Table III lists the data for this test. The results of this test showed that variation in the response of the filter papers was considerable, as shown by variations in the pickup rate. These rates have a range from four to 26 about a mean of 15.4 and a standard deviation of 5.3 micrograms per day per ppb F. Even with this degree of variation the correlation coefficient between the air concentration and the filter paper micrograms of fluoride is 0.77. This is a significant value. This correlation

further indicates that about 60% of the variation of the fluoride content of the filter papers can be related to variations of the air concentrations and 40% to other causes. While the filter papers

TABLE III.  
FILTER PAPER TESTS AT AIR STATIONS

Location	Exposure = 7 days		
	Conc. F. ppb	Filter Paper F Micrograms	Micrograms /day/ppb F
A	0.22	7	4
B	0.29	19.5	10
C	0.49	63	18
D	0.43	76.5	25
E	0.38	69	26
F	0.43	50.5	17
G	0.57	52	13
H	0.48	49	15
I	0.20	19.5	14
J	0.42	48	16
K	0.42	42	14
L	0.18	26	21
M	0.26	24.5	13
N	0.18	26	21
O	0.35	35.5	15
P	0.37	44	17
Q	0.30	28	13
R	0.31	19.5	9

usually picked up more fluoride at the locations which had the higher air concentrations, the actual responses shown in this test and in the greenhouse tests indicate that direct translation of filter paper data to air concentrations is subject to a great deal of uncertainty. Judging from comparative data on  $\text{SO}_2$  concentrations by wet and dry methods given by Meetham,<sup>5</sup> this wide variability of the filter-paper method is not unexpected.

These tests of the filter-paper sampling of fluorides indicate that an areal pattern of concentrations can be estimated as long as a relatively large number of sampling locations is used, the area is fairly uniform, and comparisons are limited to exposures during the same time period. However, the estimation of an areal pattern would have to be based upon the over-all indication of several close stations rather than upon single station values, because of the large variation which is possible in the sampling technique. The variation in response at individual locations which was observed in the present tests shows that great care should be used in drawing conclusions from successive samples. Again a relatively large number of tests should be carried out to delineate the normal variation for the region. After this is determined, conclusions might be drawn for those test periods which differ significantly from the usual or normal pattern.

MacIntire's data<sup>3</sup> also indicate variable pickup rates during different sampling periods as judged from a comparison of the ratio of the fluoride pickup of Spanish moss and limed filter paper. Within each of his tests, individual stations generally showed comparable ranks of fluoride concentration for both the moss and the papers so that the same areas of relatively high and low concentrations were indicated by both materials. However, because of apparent changes in the over-all pickup of both Spanish moss and limed paper it would not be clearly determinable how the fluoride air concentrations changed at the sampling stations from one test period to another.

#### Summary

THE RESULTS of the various tests of the filter-paper air-sampling technique which were conducted can be summarized rather

briefly. The tests show that the filter papers should not normally be expected to give a quantitative picture of fluoride air concentrations comparable with that obtained by the usual air-sampling techniques. However, in an area in which fluoride air concentrations are high, filter papers will usually pick up more fluoride than will papers similarly exposed in an area with lower fluoride air concentrations. Changes in the conditions of exposure, either in air concentrations or wind and weather conditions, apparently alter the rate at which the filter paper picks up fluoride from the air. Any variation in this pickup can introduce errors in the evaluation of the results.

It is readily apparent that the tests described in the discussion do not represent a complete analysis of the problem although they can serve as a guide to possible uses for the filter-paper technique. Some aspects of the technique, such as the relatively close agreement between papers exposed side by side over the same period, are encouraging. This indicates that the technique might be refined into a useful field technique, and even in the present stage of development it appears that qualitative, but nevertheless very useful, results can probably be obtained at a relatively low cost compared to that for conventional air sampling techniques.

#### Acknowledgments

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## THE INFLUENCE OF AEROSOLS UPON

# The Respiratory Response of Guinea Pigs to Sulfur Dioxide

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THE POSSIBLE influence of particulate matter upon the toxicity of irritant gases has been the subject of a large amount of speculation and the object of a small amount of experimental work. The problem is not only intriguing from a theoretical standpoint, but is also pertinent to air pollution toxicology. Several authors<sup>1,2,3,4</sup> have suggested that such an interaction might be one of the keys to an understanding of the complicated toxicological picture of the air pollution disasters.

The first experimental evidence that an aerosol might affect the response to an irritant gas was presented by Dautrebande in 1939.<sup>5</sup> He found that concentrations of mustard gas which were relatively harmless to rats would produce pulmonary edema and death when administered in combination with an inert aerosol. This he referred to as a "vector" aerosol and postulated that adsorption of gas on the aerosol particles had increased the amount of gas reaching the lungs. Dautrebande and Capps<sup>6</sup> and Dautrebande, Shaver, and Capps,<sup>7</sup> studying the sensory response of human subjects to constituents of the Los Angeles smog, found that the presence of aerosols of sodium chloride, oil, or smoke increased markedly the irritation produced by sulfur dioxide, formaldehyde, and other gaseous pollutants.

LaBelle, Long, and Christofano<sup>8</sup> studied the effect of aerosols on the survival time of mice exposed to formaldehyde, acrolein, and oxides of nitrogen. They then calculated from theoretical considerations the probable percent penetration of the upper respiratory tract by various gases. Know-

ing the percent penetration of aerosols of various particle sizes, they postulated that if the gas penetrated to a greater extent than the aerosol, then adsorption on the aerosol would decrease the amount reaching the lungs and the toxicity would decrease. Such a situation exists with the oxides of nitrogen which penetrate the upper respiratory tract 100%. Conversely, if the gas did not readily penetrate the upper respiratory tract, adsorption on a small aerosol would tend to carry more gas to the lungs and thus increase the toxicity. Such a situation exists with formaldehyde as only 10% of the gas normally penetrates the upper respiratory tract. Their theoretical calculations predicted their results in over 70% of their gas aerosol combinations.

Pattle and Cullumbine,<sup>9</sup> using mice, found that the presence of smoke increased the toxicity of sulfur dioxide. They believe that adsorption of gas by the aerosol need not be postulated to explain their results as the high concentration of smoke used very likely produced changes in the respiratory pattern of the animals. Gordieyeff<sup>10</sup> studied the response of rats, mice, and hamsters to various mixtures of gases and aerosols and failed to find any alteration of toxicity which he could attribute to the presence of the aerosols.

Previous work has utilized mainly mortality and/or lung pathology as a means of evaluating response, thus necessitating the use of high concentrations of irritants. A method developed recently permits the evaluation of the respiratory response of guinea pigs during exposures of an hour to relatively low concentrations of irritants.<sup>11,12</sup> The method yields a fairly complete picture of the mechanical and ventilatory changes

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in the lungs but only the increase in pulmonary flow-resistance will be considered.

This is the resistance to flow of gas in and out of the lungs and airway. An increase in resistance may in general be taken as an indication of bronchial constriction, a classical example being the asthmatic patient. We have found that both sulfur dioxide and sulfuric acid mist produce significant increases in resistance and furthermore that the magnitude of this increase is related to the concentration of irritant present. The criterion of response used throughout this paper will be the percent increase in resistance produced by an hour exposure to the substance or substances being discussed.

Two experimental approaches to the problem were used. The first was to examine the response to mixtures of sulfur dioxide and sulfuric acid mist to determine whether the response was greater than could be accounted for on the basis of simple addition. The second was to examine the effect of an aerosol of sodium chloride on the response to sulfur dioxide. In both these situations, the particle size of the aerosol would be expected to govern to a considerable extent the toxicological picture. For this reason both aerosols were studied at two different particle sizes.

When preliminary work indicated that the response to a given concentration of sulfur dioxide was greater in the presence of the vector aerosol, it was of interest to determine whether this effect would be present over a wide range of gas concentrations and, if so, whether it would be uniform throughout or would vary with the gas concentration. In an attempt to answer these questions, enough data were collected to establish a second dose-response curve for sulfur dioxide in the presence of a constant concentration of sodium chloride. Examination of the inter-relationship of the dose-response curves for sulfur dioxide alone, sulfur dioxide plus the vector aerosol, and sulfuric acid mist (as representative of an irritant aerosol) makes possible some speculations upon the toxicological mechanisms involved.

#### Methods

THE PHYSIOLOGICAL techniques have been described in detail elsewhere,<sup>11,12</sup> so will

be mentioned only briefly. Three measurements are necessary, intrapleural pressure, tidal volume, and rate of flow of gas in and out of the respiratory system. Simultaneous tracings of these three things are made. The resistance to airflow may be measured by relating the change in intrapleural pressure to the change in flow-rate at points on the tracings corresponding to equal lung volume. The resistance to airflow is expressed as cm. H<sub>2</sub>O/ml/sec.

In the experimental pattern used, respiratory measurements were made every five minutes during a control period of half an hour, then the substance under study was added to the airstream of the exposure chamber for an hour during which period respiratory tracings were again taken every five minutes. Each animal thus served as its own control. The average resistance during the control period and the resistance at the end of the hour exposure were recorded for each animal in the group and the mean of control and exposure values was calculated. The increase of the exposure mean over the control mean expressed as percent is used in the preparation of dose-response curves and in the graphical representation of the data. All statistical computations were made, however, using the actual resistance values.

The sulfur dioxide concentrations were established by metering a mixture of 1% sulfur dioxide in air from a cylinder into the airstream passing through the exposure chamber. A dual feed permitted the simultaneous addition of sulfur dioxide and aerosol to the main airstream so that mixing occurred before the air entered the chamber. Adjustment of flow-rates permitted the concentration of either to be varied independently. The sulfuric acid mist was generated by warming sulfuric acid in a three-necked flask. The vapors from the flask were swept into the main airstream by a flow of compressed air. The particle size of the mist was controlled by the temperature of the flask. The concentration was controlled by appropriate manipulation of the airflows. The sodium chloride aerosol of sub-micron particle size was obtained by the aerosolization of a 1% sodium chloride solution in a plastic Dautrebande generator\* operated at a pressure of 15 psi.<sup>13</sup>

The concentration of sulfur dioxide, sulfuric acid, and sodium chloride in the air of the exposure chamber was determined analytically during each experiment. Sulfur dioxide was determined by drawing an air sample through the hydrogen peroxide-sulfuric acid reagent of Thomas<sup>14</sup> and measuring the increase in conductivity. The sulfuric acid was measured by drawing an air sample through a type HA Millipore Filter,\*\* soaking the filter in demineralized water, measuring the conductivity, and comparing this with a standard curve. For determination of the components of a mixture of sulfur dioxide and sulfuric acid mist, the filter was placed in series with the bubbler, a method which was previously shown to give satisfactory analytical results.<sup>15</sup> A similar system was used for the mixtures of sodium chloride and sulfur dioxide.

The particle size of the aerosol was also measured during each experiment. A sample was drawn through a modified cascade impactor the fifth stage of which was a type HA Millipore Filter. The slides and filter were dropped into beakers of demineralized water and the conductivity of the resultant solutions was measured. Reference to the appropriate standard curve gave the mass deposited on each slide and the MMD of the aerosol was calculated from this by the method suggested by May.<sup>16</sup>

This method obviously leaves something to be desired in the sizing of sub-micron aerosols in which the heaviest loading is on the fifth stage. This is especially true of the aerosols from the Dautrebande generator where the specifications indicate that the largest number of particles are below  $0.1\mu$ . The average of the MMD obtained in all the sodium chloride experiments was  $0.16\mu$ , and usually 84% of the mass was below  $0.7\mu$ . Since it was not felt that the accuracy of measurement warranted a second decimal place, the figure was rounded off to  $0.2\mu$ . The method was adequate, however, to distinguish clearly between a sub-micron aerosol which would penetrate 100% to the alveoli and an aerosol of  $2.5\mu$  which would be retained largely in the upper respiratory tract and main bronchi, and it was this dis-

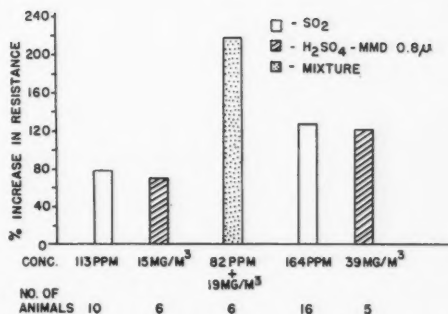


Fig. 1.  
Resistance changes produced by exposure to sulfur dioxide and  $0.8\mu$  sulfuric acid mist.

tinction which was of concern to the present work.

### Results and Discussion

THE EXPERIMENTAL design used in the studies of the toxicity of mixtures of sulfur dioxide and sulfuric acid mist was first to find a concentration of either alone which produced essentially the same degree of resistance increase. The response to a mixture of these two was then measured and compared statistically with the measured response to twice the concentration of either alone. If the response was greater for the mixture than for the higher concentrations of the constituents alone, it would suggest that the toxicity of the mixture was more than additive.

Fig. 1 shows the results of the application of this experimental design to a mixture of sulfur dioxide and sulfuric acid mist of  $0.8\mu$  MMD. The response to the mixture was greater than the response to the higher levels of either constituent alone. The actual resistance values are given in Table I. Statistical treatment of the data gave a value of  $P = 0.01$  that the response to the mixture was greater than the response to the higher concentrations of either constituent alone. Fig. 2 shows the results of an experiment of similar design using sulfuric acid mist having a MMD of  $2.5\mu$ . In this case the response to the mixture is not greater than the response to the higher levels of either alone and is even slightly less than the higher concentration of sulfur dioxide alone.

These results can be explained if it is

\*Obtained from M. L. Coenen, 28 Rue de Lessines, Brussels, Belgium.

\*\*Obtained from Millipore Filter Corp., Watertown, Massachusetts.

TABLE I.  
EXPERIMENT ON SULFUR DIOXIDE AND  
 $H_2SO_4$  MMD  $0.8\mu$

	A	B	C	D	E
SO <sub>2</sub> - PPM	113 ± 6	—	82 ± 8	164 ± 15	—
H <sub>2</sub> SO <sub>4</sub> - Mg./M <sup>3</sup>	—	15 ± 3	19 ± 3	—	39 ± 4
Number of Animals	10	6	6	16	5
Control Re- sistance cm.					
H <sub>2</sub> O/ml./sec.	0.62	0.72	0.68	0.70	0.69
Resistance - 1 hr. exposure cm.					
H <sub>2</sub> O/ml./sec.	1.11	1.22	2.15	1.58	1.52
Resistance					
Change ( $\bar{x}$ ) cm. H <sub>2</sub> O	+0.49	+0.50	+1.47	+0.88	+0.83
S $\bar{v}$ - Standard Error	0.079	0.148	0.135	0.082	0.126

postulated that there has been adsorption of sulfur dioxide by the aerosol. The smaller aerosol penetrates almost entirely to the deeper areas of the lung, hence the adsorption of gas by these particles would increase the amount of sulfur dioxide reaching the alveoli, and the response to this mixture would not be accounted for on the basis of simple addition. Palm, McNerney and Hatch<sup>17</sup> have shown that in the guinea pig about 70% of an aerosol of  $2.5\mu$  particles is retained in the upper respiratory tract. They were using inert dusts and in the case of a hygroscopic material such as sulfuric acid this percentage would be even higher. In addition, sulfuric acid of this particle size has its major effect at the level of the main bronchi rather than in the deeper areas of the lung. Thus, adsorption of the gas on this aerosol would not tend to increase the amount of sulfur dioxide reaching the lungs and one would not expect that the toxicity of the mixture would be more than additive. The fact that the response to the higher concentration of sulfur dioxide is greater than the response to the mixture suggests that possibly adsorption of gas on the aerosol has actually decreased the amount of gas reaching the lungs.

Since adsorption of the sulfur dioxide by the aerosol was postulated as the mechanism, it was of interest to examine the response to sulfur dioxide in the presence of an inert aerosol. The results of such an experiment, using a sodium chloride aerosol with a MMD of  $0.2\mu$  are shown in Fig. 3. The bar on the left is the response to sodium

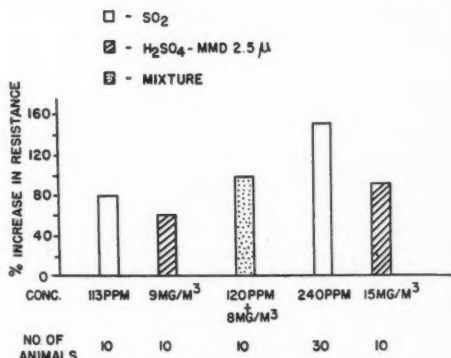


Fig. 2.  
Resistance increase produced by exposure to  
sulfur dioxide and  $2.5\mu$  sulfuric acid mist.

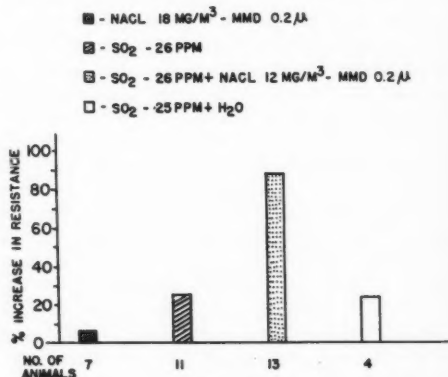


Fig. 3.  
Effect of  $0.2\mu$  sodium chloride aerosol on the  
response to sulfur dioxide.

chloride alone. The increase in resistance was very slight and was not statistically significant. The next bar shows the response to 26 ppm sulfur dioxide alone and the third shows the response to the mixture, which is definitely greater than that to the gas alone. Gordieyeff<sup>11</sup> suggests that positive results obtained in work of this type may be due to extraneous factors, among them changes in relative humidity. The operation of the aerosol generator produced no change in the relative humidity of the chamber as indicated by the wet bulb-dry bulb readings. Just as a further check on this factor, however, the aerosol generator was operated containing distilled water alone. This produced no aerosol and no

change in the response of animals to 25 ppm sulfur dioxide as shown in the bar at the right.

The presence of an aerosol of  $2.5\mu$  sodium chloride did not change the response from that observed with the gas alone as did the aerosol of  $0.2\mu$  particles. These facts again suggest that the mechanism is the adsorption of gas on the small aerosol particles and its transport to the lungs. Work reported earlier<sup>11</sup> indicated that when sulfur dioxide was given to guinea pigs through a tracheal cannula which eliminated the chance for absorption in the upper respiratory tract, the response to a given concentration was greater. This indicates that the amount of gas actually reaching the lungs is a very important factor in the degree of response resulting and that anything which will increase this penetration of gas will increase the response to a given atmospheric concentration.

The next step was to study the effect of the addition of a constant concentration of sodium chloride aerosol of  $0.2\mu$  particles to the whole range of concentrations of sulfur dioxide. The dose-response curves for the gas alone and the gas plus aerosol are given in Fig. 4. The numbers beside each point indicate the number of animals studied at each concentration. All the way along the dose-response curve the response to a given concentration of sulfur dioxide was increased by the presence of aerosol. A comparison of the two dose-response curves leads to some speculations upon the mechanisms involved.

The two curves may be compared on the basis of the concentration required to produce equal response. In other words, 250 ppm of sulfur dioxide plus aerosol produced the same response as 800 ppm alone; 100 ppm with aerosol equals 300 ppm alone and so on down the curves. The ratios of the concentrations giving an equal response are then taken, i.e., 800 ppm/250 ppm, 300 ppm/100 ppm, etc. These ratios plotted against the concentration of sulfur dioxide in the gas aerosol mixture are shown in Fig. 5. This shows that over the concentration range of 250 ppm down to around 25 ppm a given concentration of gas plus aerosol gives the same response as would be obtained with 2.5 to three times that concentration of sulfur dioxide given alone. At

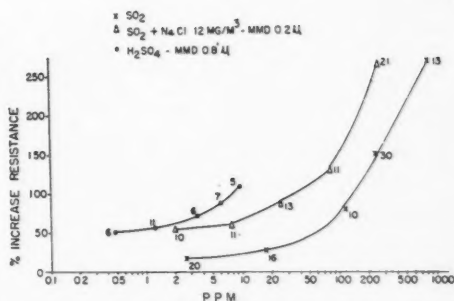


Fig. 4.

Dose-response curves for sulfur dioxide, sulfur dioxide plus sodium chloride, and sulfuric acid mist. The numbers beside each point indicate the number of animals exposed at each concentration.

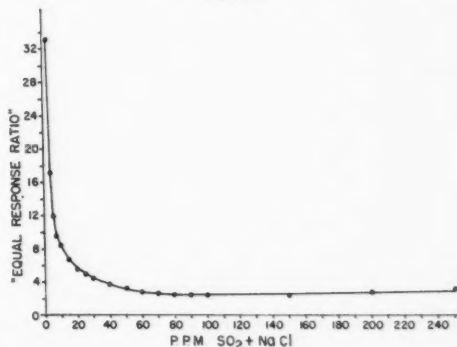


Fig. 5.

Comparison of dose-response curves for sulfur dioxide and sulfur dioxide plus sodium chloride. The "equal response ratio" is the ratio of concentrations (PPM  $\text{SO}_2$ /PPM  $\text{SO}_2 + \text{NaCl}$ ) producing the same degree of response. This is plotted against the  $\text{SO}_2$  concentration in the gas-aerosol mixture.

the very low end of the concentration scale, however, this relationship breaks down and the sulfur dioxide plus aerosol produces a response equal to around 30 times that concentration of gas alone. In other words, 2 ppm of gas plus aerosol gives a response equal to 60-70 ppm of gas alone rather than to 5 or 6 ppm as would have been predicted from the data on higher concentrations.

Vorwald<sup>2</sup> suggested that possibly the adsorption of irritant gas on an inert aerosol could convert it to an irritant aerosol which would then cause high local concentrations in the lung tissue sufficient to produce a



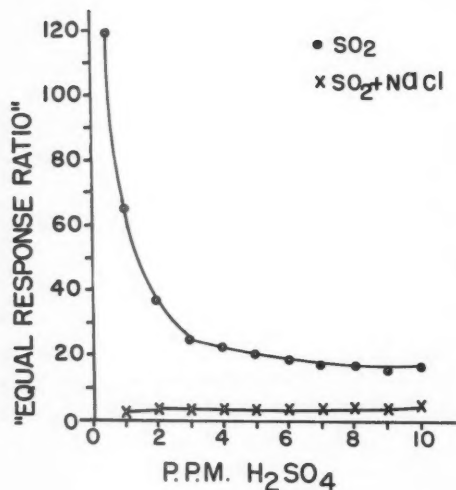


Fig. 6.

Comparison of dose-response curves for sulfur dioxide and sulfur dioxide plus sodium chloride with dose-response curve for sulfuric acid. The "equal response ratio" is the ratio of concentrations (PPM  $SO_2$ /PPM  $H_2SO_4$  or PPM  $SO_2 + NaCl$ /PPM  $H_2SO_4$ ) producing the same degree of response. These are plotted against the concentration of sulfuric acid.

response. Certainly, on a molar basis, sulfuric acid is more toxic than sulfur dioxide and the first difference that comes to mind is that the one is an aerosol and the other is a gas. The dose-response curve for sulfuric acid mist of sub-micron particle size is shown in Fig. 4. This can be compared with the curve for sulfur dioxide and with the curve for sulfur dioxide plus aerosol on the basis of concentrations producing equal response as was done before. These data are plotted in Fig. 6. In the higher concentration ranges, the sulfuric acid mist is uniformly equivalent to 15-20 times that concentration of sulfur dioxide. As the concentration reaches very low levels, however, the same phenomenon seen previously occurs and the response produced by the sulfuric acid is equivalent to the response produced by a much higher concentration of sulfur dioxide than would have been predicted from working with only the higher concentrations. In other words 0.5 ppm of sulfuric acid mist (2 mg./cu. m.) is equivalent to 60 ppm sulfur dioxide rather than to 8-10 ppm as would have been predicted.

When the sulfuric acid is compared with the sulfur dioxide plus aerosol, a straight line results and a given concentration of sulfuric acid mist is equivalent to about three times that concentration of sulfur dioxide-aerosol mixture throughout the whole range of concentrations. This seems to suggest that the gas aerosol mixture is behaving biologically as if it were an irritant aerosol.

The complete explanation for the difference in behavior at the low end of the concentration range is not clear. It does, however, indicate that the study of only high concentrations would not have predicted correctly toxicological events produced by low concentrations. If further work on other gas-aerosol mixtures substantiates this behavior, the fact could have import for air pollution toxicology which lacks as yet a clear explanation for the fact that mortality and morbidity statistics during the acute disasters are inconsistent with the recorded toxicities of the individual components.

### Summary

THE INCREASE in pulmonary flow resistance caused by an hour exposure has been used to study the response of guinea pigs to sulfur dioxide alone and in combination with sulfuric acid mist and sodium chloride aerosols. The degree of response to a mixture of sulfuric acid of sub-micron particle size and sulfur dioxide was greater than could be accounted for on the basis of simple addition. This was not the case when sulfuric acid of  $2.5\mu$  particles was used. Sub-micron aerosols of sodium chloride, inert alone, increased the response to all concentrations of sulfur dioxide studied. The potentiating effect was much greater at concentrations below 25 ppm sulfur dioxide than would have been predicted on the basis of data obtained from the higher concentrations.

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# Classification of Air Pollution Exposures

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*The concentration, averaging-time, recurrency triad is introduced and its significance and some of its properties are explained in terms of familiar air pollution incidents. From such an approach, we should be able to predict various manifestations of air pollution.*

IN THE development of a method for classifying air pollution exposures, we propose to use an approach familiar to hydrologists. Except for man's recent tinkering with cloud seeding, he has very little control over frequency and intensity of rainfall. He can merely measure it and attempt to predict what will happen in a stream or reservoir, and how often. In air pollution the sources we are most concerned with are man-made, and to an extent controllable, but nevertheless both the sources and the processes of air contamination are dynamic. In the interest of developing a methodology for approaching the dynamism of processes, we shall first set aside the dynamism of sources. Once the method is defined, we can inquire into ways of reintroducing the dynamics of source location, elevation, type, and size over all time periods of interest.

## The Dynamic Nature of Air Pollution Sources

ALTHOUGH individual communities differ in their present capacity to contaminate their ambient air environment, they, as a group, are subject to many factors tending to alter their potential to do so. Among those factors tending to increase this potential:

(a) There is a continuing trend toward increased urbanization of the world's population.<sup>1</sup> It has been estimated that whereas now 21% of the world's people live in cities over 20,000, by the year 2050 this percentage will have increased to 90%. In North America, the percentage urbanization is now 42% and is increasing year by year.

(b) The population of the United States is increasing at the rate of 14.9% per decade, and this rate of growth is likely to continue for some time to come.\* This factor, added to the preceding one, points to bigger and bigger urban complexes in the years ahead.

(c) The amount of energy expended per person is increasing yearly and shows no sign of leveling off in the foreseeable future. It has been the experience of the past that air contamination increases with increase of energy expenditure. Even the location of major units of energy production or use on the outskirts of urban areas has not solved the problem. Urban growth soon envelopes the outskirts, and air in its movements and pauses does not respect municipal boundaries.

Among the factors tending to decrease the potential of communities to contaminate their ambient air environment are:

(a) The assumption that present efforts to abate present sources by presently known methods will continue and that new control concepts will be explored and adopted.

(b) Changes in the technology of the production and use of energy may over the years replace, at a greater rate than the increase of energy expenditure, proc-

For presentation at the Annual Meeting of the AMERICAN INDUSTRIAL HYGIENE ASSOCIATION, Philadelphia, Pennsylvania, April 26, 1956.

\*Davis, Kingsley: The Origin and Growth of Urbanization in the World. *Amer. J. Soc.*, 60:5, 429 (March) 1955.

esses productive of air pollution with processes producing less or no air pollution.

(c) Development of the isolated fully automated factory, new sources of food supply, and other devices currently of science-fiction, and also the need of dispersion for civil defense, may all reverse the trend toward urbanization.

#### Air Pollution Characteristics

AS A ROUGH first approximation, one may assume that the influences of the foregoing factors tending to increase and decrease pollution are of the same order of magnitude and, therefore, tend to cancel out. Over a relatively long period of time the contributions of individual sources might change, but not the net impact of all sources of the community. This assumption is a weak one with respect to considerations of exposure to the plume from an individual stack, but a relatively strong one for the other conditions to be discussed. The above concept allows sufficient working room in terms of time to allow an initial trial of the hydrologic approach, subject to later modification to account for inequality of the expansive and diminutive factors, temporarily assumed in balance.

#### The Time-Scale of Exposures

IN WHAT follows, our concern is with the exposure of a particular location (represented by the dot on the several drawings of Fig. 1), regardless of whether at that location there be a man, a vegetable or flower leaf, a painted wall, or all three exposed to the air.

In situation I, exposure to the effluent from the chimneys at the left is intermittent, and the characteristic exposure time is of the order of minutes. In situation II, exposure to the pollution originating in the adjacent community is intermittent, and owing to a diurnal land-sea breeze regime the characteristic exposure time is of the order of hours. In situation III, exposure to contaminants originating in the community is intermittent (perhaps rare),

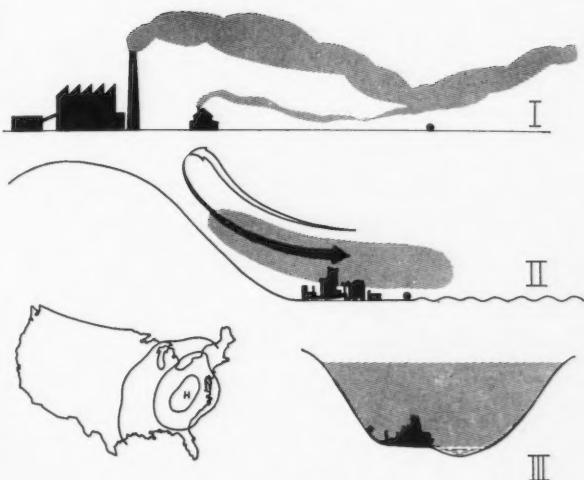


Fig. 1.

and the characteristic exposure time is of the order of days.

Because of the fluctuating character of pollutant concentrations measured "from lungful to lungful" or in similarly small volumes of air, we should expect intuitively that the characteristic concentration of pollutant is greatest in situation I and least in situation III.

#### Concentration, Averaging-Time, Recurrency

THE march of concentrations with time at the designated location may be plotted in such a way (Fig. 2) that the scale of concentration is intentionally left general, but is labeled for later use. The scale of time is unlabeled, so that we may view the whole record variously as a minute, hour, day, or even years long. An "end-to-end" series of concentration values averaged over periods of duration  $T_A$  and  $2T_A$ , together with peak values of the concentration in each time interval  $T_A$ , are indicated.

Since in the example of Fig. 2 there is a detectable concentration during each time interval  $T_A$ , it follows (Table I - Fig. 3) that the number of times the concentration is greater than detection threshold equals the number of time intervals. This would not be the case if there were time intervals during which the contaminant, if it existed in air, was below detection threshold concentration.

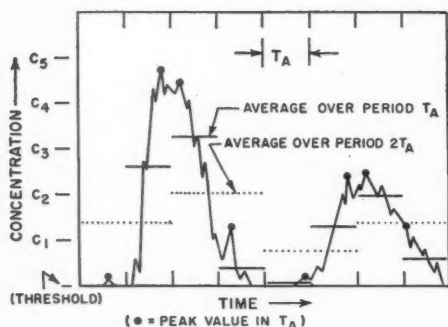


Fig. 2.

The point E (Fig. 3) represents the occurrence of a concentration, averaged over time  $T_A$ , of  $C_2$  or greater twice in eight periods of duration  $T_A$ , giving a frequency of  $2/8$  or  $0.25$ . The average recurrence period is, therefore, four  $T_A$  units; i.e., a concentration of value  $C_2$  or greater is experienced once every four  $T_A$  units of time. Because of the need to compare curves for other averaging periods on the same graph,

TABLE I.						
Number of Times Concentration is Equal to or Greater Than—						
	Detection Threshold	$C_1$	$C_2$	$C_3$	$C_4$	$C_5$
Peak concentration in $T_A$	8	6	4	2	2	0
Concentration averaged over $T_A$	8	4	2	1	0	0
Concentration averaged over $2T_A$	4	3	1	0	0	0

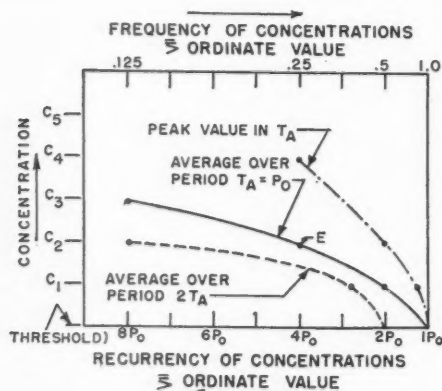


Fig. 3.

the symbol  $P_0$  is used as the time unit at the bottom of the graph.

Several noteworthy points may be mentioned here. For any constant value of average recurrence period  $P$ , the concentration-recurrence curve is lower, the longer the averaging time. Also, if for all averaging periods  $T_A$  a detectable concentration is observed, then the curve for this averaging period originates on the threshold line at a value of average recurrence period identical with that of the averaging period.

In the example (Fig. 2) all concentration values were greater than threshold; hence, the curves (Fig. 3) for averaging time  $T_A$  and averaging time  $2T_A$  extend to threshold values of concentration at average recurrence periods  $1P_0$  and  $2P_0$ , respectively. If concentrations below threshold had appeared in the "period of record" shown (Fig. 2), the point of intersection of both of these curves (Fig. 3) with the threshold line would lie to the left. The effect of the occurrence of concentrations below detection threshold is like that of using a less sensitive instrument with a higher detection threshold (Fig. 4). However, the detection threshold for average and peak values may not be the same (Fig. 5). Curve 1 obviously has a higher average value, while only curve 2 would be noticed in the record.

Finally, it is obvious (Fig. 3) that the peak value occurring in time interval  $T_A$  is essentially a different statistic. Since for each value of a peak there corresponds an average value, the curves for average

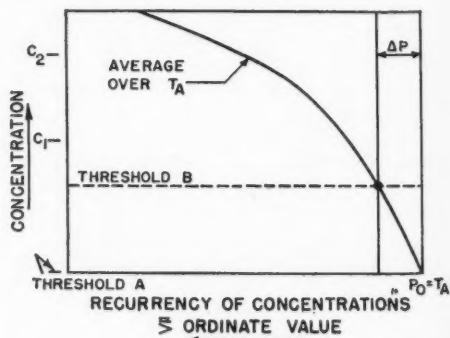


Fig. 4.



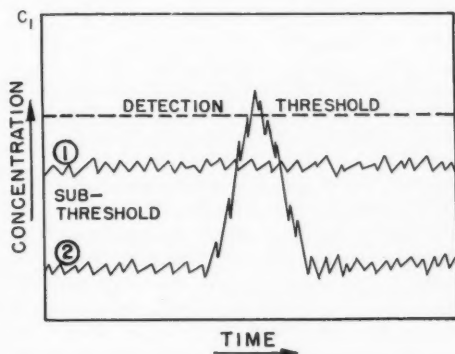


Fig. 5.

over time interval  $T_A$  and peak value in  $T_A$  are shown as intersecting at the detection threshold.

#### Generalized Air Pollution Exposure Chart

FOR ANY location, an array of data similar to Table I may be developed for  $T_A$  equal to a minute, an hour, a day, and a year, and the data may be plotted in a manner similar to Fig. 3. A chart of this type (Fig. 6) gives a guide on which different manifestations of air pollution may be located and from which certain interrelationships between problem areas and problem types may be more easily studied.

It should be emphasized at this point that data are not yet available to locate such curves accurately, nor do we understand their characteristics fully. For convenience only, the recurrence scale is logarithmic.

It may be observed that concentration values below the threshold of detection have been allowed for, since, for example, the curve for one-hour averages reaches the detection threshold to the left of the one-hour recurrence value.

The three pollution situations already discussed (Fig. 1) may be located (Fig. 6) according to their characteristic time-scale (averaging period) and their expected average recurrence time. Thus, situation III is represented on the chart as a value of two-day average concentration which might be reached or exceeded at a given location on the average once in some 10 or 20 years.

During an episode or situation like III,

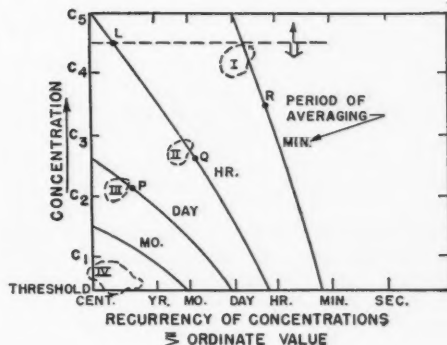


Fig. 6.

the family of concentrations measured over shorter averaging periods, e.g., one hour instead of several days, would in general vary over a range of concentration values. Thus, the highest one-hour average concentration during situation III might attain the value  $C_Q$  (point Q).  $C_Q$  may be expected to be larger than the highest one-day average concentration,  $C_P$ , and smaller than the highest one-minute concentration,  $C_R$ . It should be noted that the locus defined by III, P, Q, and R represents one particular occurrence of situation III. Moreover, *only one* of these points (III) on such a locus also represents the average recurrence time correctly. This diagram obviously would lose its utility if this feature were avoided by considering only transitional or conditional probabilities for each curve, given a particular two-day concentration  $C_{III}$ . A locus extending downward

TABLE II.

Symbol in Fig. 6	Description of Air Pollution Exposure	Prototype Incident
I	Downwash in immediate wake of a stack Morning fumigations in a valley miles from a pollution source in the same valley.	(Numerous)
II	Daytime pollution associated with diurnal variations of the wind and temperature field in a large city between ocean and mountain	Trail, B. C.  Los Angeles
III	Air contamination associated with protracted periods of air stagnation	Donora 1948; London 1952
IV	Air pollution experienced over a lifetime	(Being given special attention in research today)

and to the left of the symbol I may be analyzed in similar fashion.

Characteristic time-scales of several familiar air pollution incidents may now be located (Fig. 6) with the aid of Table II.

A diagram of this type will be valid for only one place, and therefore the diagram valid for a site in Donora would be different from that for a site in the Columbia River Valley. It should not be too difficult to develop portions of the curves characteristic for different sites, with the aid of suitable, carefully selected measurements of air quality. A few portions of the curves will have validity restricted to the concentration of a particular effluent from a particular stack. However, more generality of application is expected for other portions.

Those portions of the curves of Fig. 6 which lie to the right of a recurrence time equal to the length of available record (i.e., the period of direct measurement) can be drawn directly from the observed data. In this case, we may expect better estimates of average recurrence time when shorter periods of averaging are of interest (curves at the right in Fig. 6). As our interest extends to periods of averaging or recurrence times similar to or greater than the length of the available record, we must look for characteristic frequency distribution laws that will permit extrapolations beyond the period of record.

It is emphasized that such diagrams are applicable to a place *affected by* air pollution rather than to a source of air pollution. This approach differs from the one prevailing today, which concerns itself mainly with the life history of the plume from a particular stack. One learns from the latter approach that the "maximum" concentration should have a certain value. However, from a practical point of view it is more important to know *how often* at some point or points the concentration may attain some given fraction of this "maximum," and to know this *for different averaging times*.

#### Reintroduction of Dynamism of Sources

THE CURVES herein presented are all restricted to the static situation of sources remaining the same over the longest time

scale of the chart. Since this is obviously not the case in practice, they must be further studied to determine how they can be made to reflect an increase or decrease of source potential. One means of so doing is illustrated by the horizontal line through point L on Fig. 6, which can be taken as marking the maximum concentration that could possibly occur from the sources existing at the time of chart preparation. With such a line on the chart, the portions of the family of curves above the line have no meaning, since they represent an impossible condition. Therefore an effect of source attenuation is to lower this line, and of source increase to raise it.

#### Extrapolation of Curves as a Prediction Device

WHAT LED the authors into this excursion into methodology was the claim of hydrologists to be able to predict from a statistical treatment of five or 10 years past rainfall and stream-flow data, as an example, the peak 30-minute river crest occurring in the next 100 years. What is being sought is a similar basis for the prediction of air pollution incidents by the extrapolation into the future of a few years' records of air analysis at a few points within an area. The first point to stress is that we may try this approach now with existing records. The second point of importance is to so plan future air pollution studies that the resultant data can most readily be converted to this or some better scheme for analysis and prediction.

#### Conclusion

THE CONCENTRATION, averaging-time, recurrence triad has been introduced, and its significance and some of its properties for air pollution have been explained. Application has been made to familiar air pollution incidents of the past. It is suggested that research efforts employing the triad approach require enlargement, if not stimulation, in order to improve our ability to assess the kind of air environment toward which communities are now tending, and in the expectation that short-term methods of assessing long-term effects will eventually become successful.

## THE DETERMINATION OF

# Lead in Air and in Biological Material

—Modification of the American Public Health Association's Method—

PATRICIA A. MECHERLY, A. LILLY and N. E. WHITMAN  
Industrial Hygiene Division, Bethlehem Steel Company  
Bethlehem, Pennsylvania

THE FOLLOWING method for the determination of lead in air and in biological materials was developed in Bethlehem Steel Company's Industrial Hygiene Laboratory for the purpose of increasing both the speed and the accuracy of the procedure previously in use. The earlier method was a visual color comparison based on the A.P.H.A. dithizone method.<sup>1</sup>

### Preparation of Glassware

ALL glassware used in this lead method should be delead by rinsing with nitric acid (minimum of 30% by volume) and then with distilled water.

### Special Apparatus

THE digestion and extraction apparatus as pictured and described in Fig. 1 was fabricated especially for this laboratory by Fisher Scientific Company.

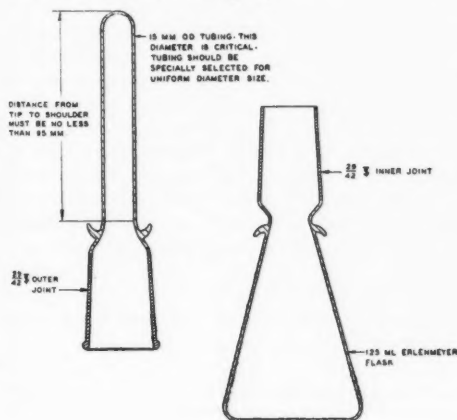


Fig. 1.

Digestion and extraction apparatus.

### Preparation of Reagents

ALL the chemicals used in this method are of reagent grade which meet ACS specifications.

**DITHIZONE**—Dissolve 25 milligrams of diphenylthiocarbazone (Eastman Kodak #3092 or the equivalent) in one liter of chloroform.

**AMMONIUM CITRATE**—Dissolve 430 grams of ammonium citrate, dibasic, in 500 ml of distilled water and add sufficient ammonium hydroxide to make the solution definitely alkaline to phenol red (pH 8 approximately). Dilute the solution to one liter and purify by extracting with 100 ml portions of the chloroform dithizone solution until no further color change is noted in the dithizone layer. Wash the citrate solution with pure chloroform to remove any residual dithizone.

**HYDROXYLAMINE HYDROCHLORIDE** — Dissolve 20 grams of hydroxylamine hydrochloride in approximately 50 ml of distilled water and add sufficient ammonium hydroxide to make the solution definitely alkaline to phenol red. Purify this solution by extracting with the chloroform solution of dithizone as described earlier in the preparation of ammonium citrate solution. After purification make the solution just acid to phenol red with hydrochloric acid and dilute to 100 ml.

**POTASSIUM CYANIDE**—Dissolve ten grams of lead-free low-sulfide potassium cyanide\* in distilled water and dilute to 100 ml.

**STANDARD LEAD SOLUTION**—Prepare a

\*The sulfide concentration should be as low as possible since lead which is present as the sulfide will not react with dithizone. Concentrations of sulfide as low as 0.003% in the potassium cyanide have noticeably interfered in the dithizone determination of lead.

stock solution by dissolving 1.5984 grams of lead nitrate in one liter of 10% nitric acid (one volume of 69 to 70%  $\text{HNO}_3$  to nine volumes of distilled water). One milliliter of this solution will contain 1.0 mg Pb. From this stock solution prepare by dilution with 10% nitric acid a solution containing 0.020 mg Pb per 1 ml. From this second solution prepare by dilution with 10% nitric acid a series of standards containing 1, 3, 5, 7, and 9 micrograms Pb per 5 ml respectively.

#### Preparation of Samples

**AIR SAMPLES**—Remove air sample from impinger flask, electrostatic precipitator tube, etc., in the usual manner, being careful to evaporate off all alcohol used before continuing with the dissolving of the sample. Dissolve the sample by heating with 10 ml of nitric acid and dilute to 100 ml with distilled water. Use a suitable aliquot for analysis.

**SAMPLES COLLECTED ON SULFURIC ACID DIGESTIBLE FILTERS AND BULK SAMPLES OTHER THAN BIOLOGICALS**—Place filter containing the sample or a weighed quantity of the bulk material in the flask section of the digestion and extraction apparatus; add 10 ml of sulfuric acid and heat; add with caution 1 or 2 ml portions of nitric acid until digestion is complete and a clear or light yellow solution is obtained. If digestion is difficult, add with extreme caution a drop or two of perchloric acid. When digestion is complete, place in a muffle oven at 500°C for 30 minutes, cool, add 5 ml of 10% nitric acid, heat to dissolve all salts and dilute to 100 ml with distilled water. Use a suitable aliquot for analysis.

**BLOOD SAMPLES**—To a maximum of 20 grams of whole blood in the flask section of the digestion and extraction apparatus add 20 ml of nitric acid (smaller amounts of blood require smaller amounts of acid) and evaporate to dryness.\* Add 10 ml of sulfuric acid and heat until a clear yellow solution is obtained. A few drops of perchloric acid may be added cautiously to complete the sulfuric acid digestion. When digestion is complete, place in a muffle oven at 500°C for 30 minutes to fume off excess

sulfuric acid and to remove the last traces of organic material.

**URINE SPECIMENS**—Measure and record the total volume, specific gravity, and temperature of the urine specimen.\*\* Add 10 ml of nitric acid to the empty specimen bottle and rotate the bottle so that the entire inner surface is wet with the acid. Return the specimen to the specimen bottle, mix and place a 50 ml aliquot of the acidified specimen in the flask section of the digestion and extraction apparatus. Add 10 ml of nitric acid and evaporate to dryness.† Add 2 ml of sulfuric acid and heat until a clear colorless or straw colored solution is obtained. When digestion is complete, place in muffle oven at 500°C for 30 minutes.

#### Analysis of Samples

**TO THE flask** containing either the ashed biological sample or an aliquot of the solution of the air or bulk sample add 5 ml of 10% nitric acid and heat to dissolve all salts. Add 15 ml of the ammonium citrate solution and make just alkaline to phenol red with ammonium hydroxide. Add one ml of hydroxylamine hydrochloride solution, 5 ml of potassium cyanide solution, and 5 ml of the chloroform solution of dithizone in that order, mixing well after each addition. Cap the digestion flask with the extraction tube portion of the digestion and extraction apparatus and shake the apparatus vigorously for 30 seconds. Invert the apparatus and allow 15 minutes for the chloroform layer to settle to the bottom of the extraction tube. Measure the percent transmission of the chloroform layer by inserting the extraction tube in the cell compartment of a colorimeter or photometer which is equipped to handle a 15 mm O.D. test tube (a Beckman Model C colorimeter with a green, Corning 4010, filter was found to be satisfactory). Convert this percent transmission reading to micrograms of lead by comparing with a standard curve.

#### Preparation of Standard Curve

**ADD 5 ml aliquots of standard lead solutions** containing 0, 1, 3, 5, 7, and 9

\*If excessive foaming occurs during evaporation and digestion of blood or urine samples, a drop of 2-Octanol (Eastman Kodak #66) will help control it.

†If excessive foaming occurs during evaporation and digestion of blood or urine samples, a drop of 2-Octanol (Eastman Kodak #66) will help control it.

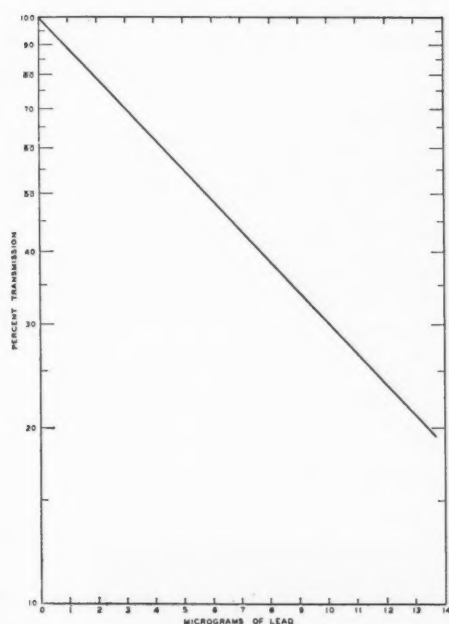


Fig. 2.  
Standard curve.

micrograms of lead per 5 ml respectively to flask sections; treat, extract and read in colorimeter exactly as described under "Analysis of Samples" above. Plot percent transmission against micrograms of lead on semi-logarithmic graph paper. See Fig. 2.

### Discussion

**TIME SAVINGS EFFECTED**—It was found that an overall saving in time of approximately 25% was effected by adopting this method modification. The time required for preparation and ashing of samples remained the same, but time was conserved by eliminating the transfer from ashing beaker to separatory funnel and by reading percent transmission directly in the colorimeter rather than estimating the mixed color by visual comparison with a set of standards. A quite significant amount of time was also saved in the clean up and glassware preparation steps since the two piece digestion and extraction apparatus replaced both the ashing beakers and the separatory funnels, the last of which had been quite troublesome due to the need for frequent lubrica-

tions of the stopcocks to prevent leakage during analysis.

**INCREASE IN ACCURACY**—A number of urine lead samples were pooled and mixed. Three 50 ml aliquots were analyzed by the visual method and three by colorimeter to estimate the background lead concentration. Varying amounts of the standard lead solution were then added to two similar series of 50 ml aliquots of the pooled urine. One such series of knowns was analyzed by the visual method and one by the colorimeter. Inspection of the data below shows that the colorimeter is somewhat more accurate and precise than the visual procedure. In addition, the average ratio of the amount found to the amount known or calculated to be present and the standard deviation for a single analysis were calculated according to Youden.<sup>3</sup> These data serve to confirm the subjective impression that the colorimeter is slightly but definitely superior to the visual method of lead estimation.

TABLE I.  
VISUAL METHOD

Blank Pb	Pb Added	Calculated Pb Conc. of Aliquot	Pb Found	Ratio of Pb found to Pb calculated
3.0	1.0	4.0	4.5	1.125
3.0	1.0	4.0	4.0	1.000
3.0	3.0	6.0	8.5	1.419
3.0	3.0	6.0	6.5	1.083
3.0	5.0	8.0	9.0	1.125
3.0	6.0	9.0	9.0	1.000
3.0	7.0	10.0	9.5	.950
3.0	9.0	12.0	10.0	.833
3.0	9.0	12.0	10.5	.874
3.0	15.0	18.0	17.0	.944

Average ratio 1.035

Slope of curve (lead calculated vs. lead found)  $b = 0.796$

Zero intercept of curve  $a = 1.72$

Standard deviation for a single analysis = 1.14

TABLE II.  
COLORIMETER

Blank Pb	Pb Added	Calculated Pb Conc.	Pb Found	Ratio of Pb found to Pb calculated
3.2	1.0	4.2	4.0	.952
3.2	1.0	4.2	3.7	.882
3.2	3.0	6.2	6.0	.968
3.2	3.0	6.2	6.5	1.048
3.2	5.0	8.2	8.6	1.049
3.2	6.0	9.2	8.9	.968
3.2	7.0	10.2	10.5	1.029
3.2	9.0	12.2	11.7	.954
3.2	9.0	12.2	12.0	.983
3.2	15.0	18.2	17.8	.978

Average ratio .982

Slope of curve (Pb calculated vs. Pb found)  $b = 0.983$

Zero intercept  $a = 0.03$

Standard deviation for a single analysis = 0.304



A comparison of the visual and colorimeter methods of estimating lead concentrations was made using pooled blood samples in place of pooled urine samples and essentially the same result was obtained. The colorimeter proved to be slightly but definitely superior to the visual method of lead estimation.

#### Other Applications

THE DIGESTION and extraction apparatus used in this method and pictured and described in Fig. 1 was found to be quite useful in other analytical methods which

required the measurement of a colored compound which was extracted from an aqueous solution by a heavier than water solvent.

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Dr. Carey P. McCord, at right, receiving a certificate of Honorary Membership in the American Industrial Hygiene Association from the President, Dr. Lester V. Cralley.

# Hydrocarbon Synthesis in Combustion II

## —LIQUID FUELS—

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JEROME F. THOMAS, Ph.D., Assistant Professor of Sanitary Chemistry

ELDON N. SANBORN, M.S., Graduate Research Chemist

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Sanitary Engineering Research Laboratory

University of California, Berkeley

THIS is part of a long range study on the combustion of fuels<sup>1,2,3</sup> and initiates the laboratory work on liquid fuels. The primary purpose of the overall study is to determine what particulate organic materials are common to both combustion effluents and polluted atmospheres and to identify them. The interest in the particulate component has been reviewed in earlier papers.

Previously reported results showed almost complete agreement in the analysis of the particulate organic material found in atmospheric samples and the analysis of laboratory samples obtained by the controlled combustion of gaseous fuels.

Before any correlation of results can be made between the various types of fuel, it is necessary to review several salient concepts from preceding studies. Particulate organic material is defined as the ether soluble portion of the total particulate matter which can be removed from a combustion effluent or a polluted atmosphere using conventional small particle filtration techniques. The residue of the ether extract is primarily soot particles and comprises the major weight of the total particulate material. Secondly, the gaseous fuels were all burned under conditions of complete and incomplete combustion as previously defined. Agreement in the analysis was obtained only when the fuels were burned under conditions of incomplete combustion.

Complete combustion resulted in the total absence of any material of a particulate nature. Thirdly, the ultimate separation into pure components was dependent on paper chromatographic techniques and even though many of the individual compounds were not identified, the similarity in chromatogram patterns indicated composition agreement between samples obtained from the atmosphere and from the laboratory furnace stack effluent. The conclusion reached was that the incomplete combustion of any carbonaceous gaseous fuel could be responsible for a portion of the particulate organic material present in the polluted atmospheres.

As mentioned, this phase of the overall study is concerned with liquid fuels, the primary objectives being the same as those previously stated. Results obtained from preliminary laboratory experiments on liquid fuels indicated a disagreement with the results obtained from gaseous fuels. In these experiments several liquid hydrocarbons, i.e., cyclohexane, 2,2,4-trimethylpentane, n-hexane, and toluene were burned in a simple alcohol lamp, using a fiberglass wick. The lamp was mounted in a stack, pure air being introduced at the base of the stack. The combustion effluents were sampled from the top of the stack by conventional means. The particulate organic material obtained from the effluent sample was subjected to the chromatographic separations, and the results were compared to those obtained from gaseous fuels. Discrepancies were immediately apparent in that there were missing bands in several chromatogram patterns. This would indicate the absence of compounds or the re-

Presented at the Eighteenth Annual Meeting of the American Industrial Hygiene Association, Toxicology Section, St. Louis, April 25, 1957.

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duction in concentration below observable limits.

One possible explanation for the absence or reduction in concentration of certain compounds includes a consideration of the reaction mechanism involved in the production of complex organic compounds from simple hydrocarbon fuels during the combustion process. A tentative mechanism has been proposed<sup>1</sup> in which simple one and two-carbon free radicals are initially produced during the combustion process. These in turn recombine through several possible stepwise processes to form the complex polynuclear aromatic hydrocarbons and their derivatives, which are the principle compounds comprising the particulate organic material. The activation energy required to initiate these reactions is thermally furnished in the flame. The amount of particulate organic material produced is thus dependent on the thermal energy available. In the combustion of liquid fuels in the manner described, a part of the thermal energy is required to vaporize the liquid fuels, leaving, on a relative basis, a smaller amount available to initiate the reactions leading to the production of the complex hydrocarbons.

It is also conceivable that there are several competing reactions in the overall mechanism with the end products being a function of a number of unknown variables. This explanation has been substantiated by two observations made in the study of gaseous fuels: (1) The same compounds were always produced regardless of the fuel but relative concentrations varied between different fuels. (2) During the combustion of any fuel at a given flow rate, the production of particulate organic material varied inversely with the flow rate of secondary air within a fourfold increase relative to the flow rate of the fuel. The total particulate material remained relatively constant. Increasing the flow rate of secondary air apparently removed the reactants from the reaction zone and simultaneously lowered its temperature.

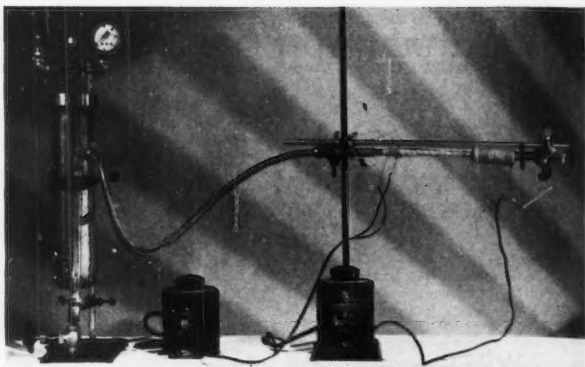


Fig. 1.  
Burner and preheater for liquid fuels.

It was felt that the discrepancies between results from liquid and gaseous fuels were variations from generalities and were due to limitations inherent in the preliminary combustion procedures on liquid fuels. Subsequent work which is herein described has shown that liquid fuels can be burned in a manner that will produce results comparable to those obtained from gaseous fuels. This was initially indicated by sampling the exhaust of an internal combustion engine, using a liquid fuel, gasoline. The results obtained from the engine exhaust sample were similar to those obtained from the gaseous fuels. From this it was assumed that if liquid fuels were burned under conditions to satisfy the activation energy, the results would be generally comparable.

#### Experimental Procedures

THE ENERGY requirements were partially satisfied by converting the liquid fuel to a gaseous state prior to ignition. This was accomplished by forcing the liquid through a needle valve into an electrically preheated chamber preceding the burner. Thermocouple stations along the preheater and burner inlet indicated when a relatively constant temperature was being maintained throughout the flowing gas phase. The temperature was arbitrarily adjusted to approximately 300° F which is below the cracking temperature of all fuels used in the investigation. The apparatus for accomplishing this is shown in Fig. 1, including

the burner which normally is mounted inside of the furnace. The furnace and sam-

pling technique have been described previously<sup>2</sup> and are identical to those used in the study of gaseous fuels.

The separation of the particulate organic material, from a combustion effluent, into broad solubility classifications has been described.<sup>3</sup> The four fractions obtained are neutral hydrocarbons and phenolic, carboxylic and nitrogenous derivatives of the neutral hydrocarbons. The polyfunctional compounds were classified with the solubility group into which they separated. The nitrogenous derivatives could be obtained only from nitrogen containing fuels and polluted atmospheres. As most of the fuels under investigation were pure hydrocarbons, very little emphasis was placed on the nitrogenous derivatives.

Descending strip chromatograms of the neutral hydrocarbons were obtained by applying aliquots of an ether solution, containing 10-15 micrograms of material per aliquot, to number 44 Whatman filter paper. The chromatograms were developed for about 18 hours, using a 40% acetic acid solution as the developing agent. The results obtained from representative liquid as well as gaseous fuels show in Fig. 2.

The chromatograms of the phenolic and carboxylic derivatives, shown in Fig. 3 and 4, were developed in a similar manner but using a 1% solution of sodium hydroxide for the developing agent.

The chromatograms of the derivatives do not show resolution to pure components as each chromatogram band is generally a mixture of what is thought to be isomers. These may be separated to pure components by eluting a number of corresponding

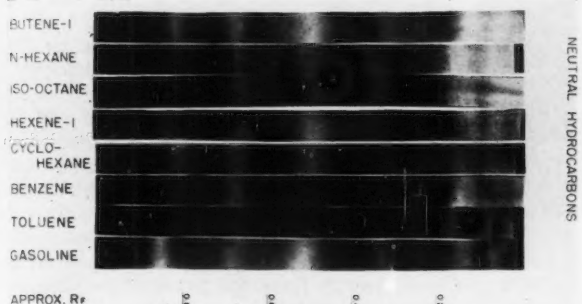


Fig. 2.

Descending strip chromatograms of neutral hydrocarbons from liquid fuels, developed with 40% acetic acid.

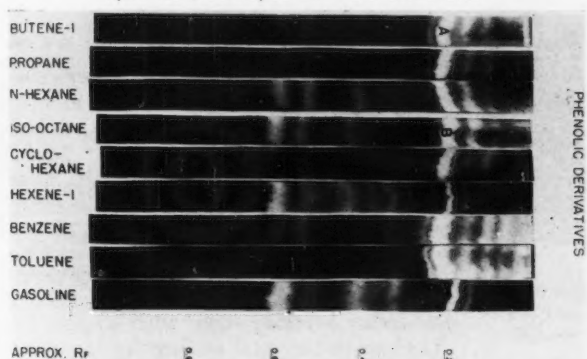


Fig. 3.

Descending strip chromatograms of phenolic derivatives from liquid fuels, developed with 1% sodium hydroxide.

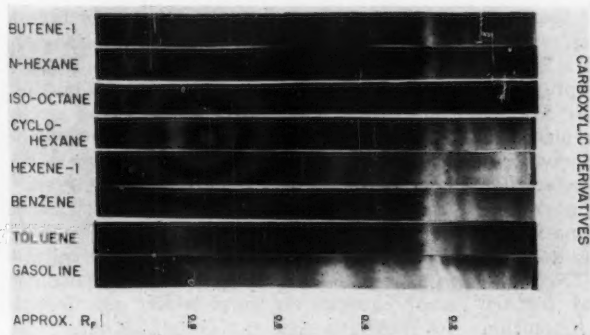


Fig. 4.

Descending strip chromatograms of carboxylic derivatives from liquid fuels, developed with 1% sodium hydroxide.



Fig. 5.

Two dimensional chromatogram of band B from 2,2,4-trimethylpentane, developed with 40% acetic acid and 20% ammonium hydroxide. Note multiple separation.



Fig. 6.

Two dimensional chromatogram of band A from butene-1, developed with 40% acetic acid and 20% ammonium hydroxide. Note multiple separation.

bands and rechromatographing the concentrated extract.

To exemplify this latter technique approximately 40 chromatograms of the fraction containing phenolic derivatives obtained from the combustion of 2,2,4-trimethylpentane, a liquid fuel, were prepared. An arbitrary band, marked B in Fig. 3, was cut from each chromatogram, placed in an acid solution and the phenolic derivatives extracted into diethyl ether. In a similar manner the corresponding band, marked A in Fig. 3, for a gaseous fuel, butene-1, was placed in an ether solution. Thus a group of similar phenolic components from two different fuels were available for further separation. A concentrate of each solution was applied to separate sheets of filter paper and a two-dimensional chromatographic technique was used for the ultimate resolu-

tion. The two developing solutions in order used were 40% acetic acid and 20% ammonium hydroxide solution. The resulting chromatograms are shown in Figs. 5 and 6. Of the several components detected by this separation, corresponding ones labelled I and II were further considered.\*

Although chromatogram position and fluorescent color strongly suggests that components I and II are identical, further confirmation was obtained by running both the ultraviolet absorption curve and the fluorescent emission spectrum of the two spots. The technique for obtaining this information directly from the paper containing the chromatographed spots of the pure components has been described.<sup>3</sup> (The apparatus used to obtain the fluorescent curves is iden-

\*The photographs of the chromatograms, shown in the various figures, have been made using a technique previously described.<sup>2</sup> It involves photographing the fluorescence excited by short wave ultraviolet radiation. Because of varying pastel colors and filter requirements, some detail of the chromatograms is lost in the photographic process.

TABLE I.  
PROPORTIONS OF EXTRACT TO SOOT FROM  
INCOMPLETE COMBUSTION

Fuel	Burning in furnace*		Burning in alcohol lamp	
	Secondary Air wt.	Extract wt.	Extract wt.	Soot wt.
Natural gas**	25.0	1		
		8.4		
Butene-1**	25.0	1		
		7.7		
N-hexane	17.6	1	1	
		4.3	165	
Cyclohexane	16.6	1	1	
		15.5	79	
2,2,4-trimethylpentane	17.3	1	1	
		4.1	57	
Hexene-1	17.1	1		
		4.0		
Toluene	15.9	1	1	
		4.4	7.5	
Benzene	15.8	1		
		9.3		
Gasoline (50 octane)	16.8	1		
		2.6		
Air Sample (Nov. 1956)	—	1		
		8.2		
Air Sample (Dec. 1956)	—	1		
		5.1		

\*All combustion in the same burner.

\*\*Gaseous fuels.



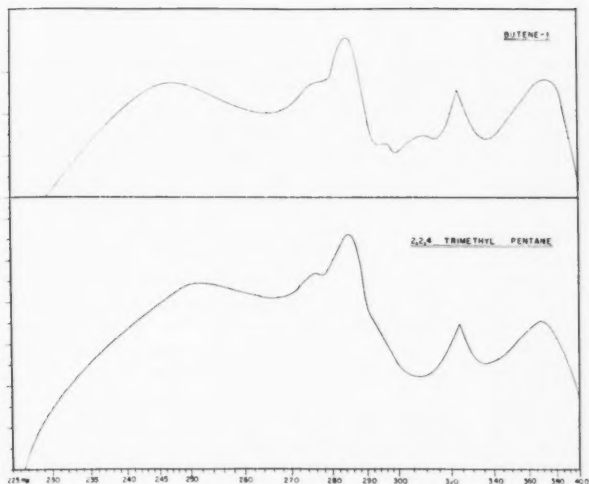


Fig. 7.

Ultraviolet absorption curves of identical phenolic component from butene-1 and from 2,2,4-trimethylpentane.

tical in principle to the new fluorescent attachment for the Beckman Spectrophotometer, Model DK2.)

Fig. 7 shows the smooth ultraviolet absorption curves of the comparable components. Fig. 8 shows the fluorescent emission curves of the same components I and II in acid and in basic condition.

Since it had been observed that the amount of particulate organic material varied under different circumstances and with different fuels, a gravimetric quantitative procedure was applied to many of the laboratory and air samples to estimate the weight of organic material to the weight of other filtered particulate material. In Table I are shown the ratios of extract to soot for liquid and some gaseous fuels.

### Discussion

FROM the study on gaseous fuels it was determined that particulate organic material found in polluted atmospheres was identical to that found in the combustion effluent of any gaseous fuel burned under conditions of incomplete combustion. Assuming the initial work on gaseous fuels acceptable, it was felt in this phase of the work that generalizations could be made on a comparative basis between liquid and gaseous fuels.

It is possible to utilize a wider variety of chemical types of liquid fuels than gaseous fuels. The gaseous fuels investigated were all simple hydrocarbons having four or fewer carbon atoms, saturated to various degrees: alkanes, alkenes, and alkynes being represented. Smoking tendency was the criterion in their selection. The variables relating total particulate material to the organic particulate material are still unknown, but the initial work did indicate very little relationship between smoking tendency and particulate organic material.

It was possible to select representative pure liquid fuels on a more logical basis. Of four major classes of hydrocarbons, at least one of each was selected for combustion with occasional duplications in class to verify results. N-hexane and

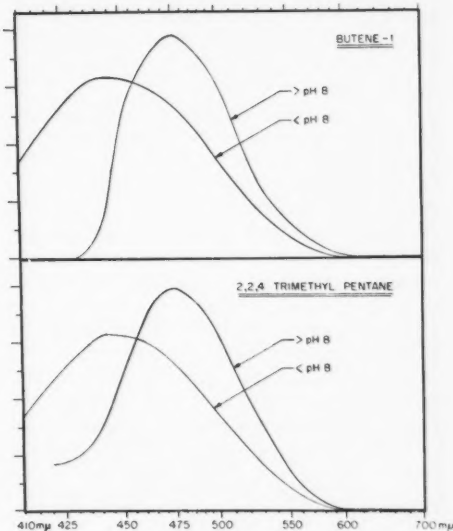


Fig. 8.

Fluorescence emission of identical phenolic component from butene-1 and from 2,2,4-trimethylpentane. Note color shift with change in pH.

2,2,4-trimethylpentane (iso-octane) are saturated aliphatic hydrocarbons; hexene-1 is an unsaturated aliphatic hydrocarbon; cyclohexane a cyclic non-aromatic; and benzene and toluene are aromatic. One mixed hydrocarbon, low octane gasoline, was also used. All of the liquid fuels burned with equal facility, although it was noted that the aromatics burned with a smokier flame. Thus, the aromatic hydrocarbons produced more particulate organic material relative to fuel consumed.

The combustion effluent of the liquid fuels was compared to that of the gaseous fuels by means of the chromatograms shown on Figs. 2, 3, and 4. The comparison was made on general pattern of separation rather than on resolution of the chromatogram to pure components. A pattern is as significant because only a small number of the combustion products have been identified. For example, the chromatograms of Fig. 2 of the neutral hydrocarbons were developed with 40% acetic acid which separated only the low molecular weight hydrocarbons. Thus, the patterns are not a complete resolution of components but they do indicate a similarity in results. Separations to pure components have been made as spot checks and show the same identity of end products. The work entailed is very extensive and is continuing.

Variations in the chromatograms indicate that certain fuels show omission or addition of bands from the general pattern, but these are the exception and no attempt will be made at this time to explain their presence or absence. On the chromatograms of the neutral hydrocarbons as well as of the derivatives, no attempt has been made to include absolute  $R_f$  values. An approximate scale is included on all the figures to enable an estimation of values. It was found that a standardized temperature was very important in developing chromatogram patterns of these hydrocarbons and their derivatives. Even slight variations in temperature can cause the general pattern to spread considerably with several components bunching at the front.

The phenolic and carboxylic derivatives, shown on Figs. 3 and 4, likewise do not show complete resolution to pure compounds but rather a general pattern. Spot checks to pure components and a comparison of

these chromatograms led to the same generalizations arrived at from the patterns. On the actual chromatograms it is difficult to note anything but the most minor variations in the separations obtained from the various fuels. It should be mentioned that with the phenolic and carboxylic derivatives it is possible by means of a two dimensional technique to separate the mixtures into approximately 38 pure components each. This is accomplished, using the technique illustrated in Figs. 5 and 6. Thus, it is apparent on the descending type chromatograms shown on Figs. 3 and 4 that many, if not all of the chromatogram bands, are composites of several compounds.

Although it is not possible at this time to identify many of the pure components it is possible to show that they are identical regardless of the fuel from which they are produced. This is illustrated by the procedures which lead to Figs. 5, 6, 7, and 8 for a gaseous unsaturated hydrocarbon and for a liquid saturated hydrocarbon. Among the more than 90 individual chemicals which can be separated by these procedures are: anthracene; phenanthrene; pyrene; fluorenone; 1,2-benzanthracene; naphthacene; 3,4-benzpyrene; 1,2,5,6-dibenzanthracene; alpha naphthol and beta naphthol. There has been no attempt in the course of this present study to identify further materials.

It has thus been shown that the products of incomplete combustion of representative liquid and gaseous fuels are essentially identical. On the basis of previous results it is assumed that a similar conclusion can be drawn between the results obtained from a polluted atmospheric sample and those of liquid fuels.

Although a nitrogen-containing fraction can be separated from the particulate organic material of polluted atmospheres,<sup>3</sup> a similar fraction did not result from burning pure hydrocarbon fuels. Apparently there was insufficient energy for nitrogen fixation during the combustion process, and any such product must be the result of some other reaction involving nitrogen contained in the fuel. The only mixed hydrocarbon fuel used in this series of experiments, non-leaded low octane gasoline, when burned in the same manner as the others, produced copious quantities of particulate organic material containing a small amount

of material whose properties indicated the presence of nitrogeneous compounds. The neutral, phenolic and carboxylic derivatives of this liquid fuel are shown on Figs. 2, 3, and 4. Another indication of the similarity of particulate organic production between gaseous and liquid fuels is indicated in Table I. There it is noted that when burned under similar air to fuel ratios, and in all cases with some slight excess air, the relative by-product yield of extractable organic material to soot is similar with a variety of fuels, both liquid and gaseous. The same parameter for two high-volume atmospheric samples falls in the same range.

The specific differences between fuels in this regard is possibly fortuitous or may be related to the structure of the fuel itself. At any rate, it is evident that the presence of cyclic structure in the fuel has little bearing on the yield of particulate organic material, much of which is aromatic.

Although no attempt has been made further to elucidate the mechanism of formation of high molecular weight organics from the incomplete combustion of relatively simple hydrocarbons, the presumption still remains that a series of cracking and reforming processes takes place in the thermally energized reaction zone of the flame. Associated with several conclusions from this present series of studies is a corollary postulation: That a large number and variety of volatile organics containing carbon, hydrogen and oxygen may be produced and released in the by-products of incomplete combustion. These would be intermediates in the cracking and reforming processes mentioned above.

## Conclusions

1. INCOMPLETE combustion of a wide variety of liquid fuels (saturated and unsaturated aliphatic, cyclic and aromatic hydrocarbons) can result in the formation of particulate organic material common to a polluted atmosphere.

2. More than 90 components, separable by standard organic procedures and paper chromatography, are present in the by-products of incomplete combustion. They include polynuclear aromatic hydrocarbons and their phenolic and carboxylic derivatives. Some of these are known toxic materials.

3. In general, the difference between liquid and gaseous fuels in the ease with which they yield the particulate organic by-products of combustion is that the former require a relatively larger amount of thermal energy to activate the reaction mechanisms. The effects of temperature and reaction time require further study.

4. Only one liquid fuel, a low-octane gasoline, produced nitrogenous particulate organic material. This is thought to result from the presence of nitrogen in the fuel and not from nitrogen fixation from air.

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## Proceedings of Health Physics Society

THE First Annual Meeting of the Health Physics Society was held on June 25-27, 1957. The Proceedings of the meeting are now available for purchase. A number of abstracts and approximately 35 complete papers are included. The price is \$3.00 per copy. Orders should be sent to C. C. PALMITER, Radiation Control Service, School of Public Health, University of Michigan, Ann Arbor, Michigan.



# HYGIENIC GUIDE SERIES

## VANADIUM PENTOXIDE

### I. Hygienic Standards

A. RECOMMENDED MAXIMUM ATMOSPHERIC CONCENTRATION (8 hours): 0.5 mg vanadium pentoxide per cubic meter of air ( $\text{mg}/\text{m}^3$ ).<sup>1</sup>

- (1) *Basis for Recommendation:* Animal experimentation,<sup>5,7</sup> and industrial experience.<sup>2,6</sup>

#### B. SEVERITY OF HAZARDS:

- (1) *Health:* Moderately hazardous for both acute and chronic exposures. Effects are chiefly severe irritation of the eyes, throat, and respiratory tract resulting in conjunctivitis, nasal catarrh, irritation of throat (atrophic pharyngitis), bronchopneumonia and mild chronic bronchitis.<sup>6</sup> Eczematous lesions of the skin and discoloration of the tongue may also occur. Prognosis is favorable. Chief complications are slight to moderate chronic changes in mucous membranes of the respiratory tract (pharynx), pneumonitis, and allergy. Questionable fibrosis and emphysema has been reported after exposure of several years.<sup>10</sup>

- (2) *Fire:* Itself, non-flammable, but may, through oxidative catalysis, cause combustion of readily oxidizable material.

C. SHORT EXPOSURE TOLERANCE: Fatal dose for man is reported to be 60-120 mg. The acute lethal dose by vein for laboratory animals is from 12-20  $\text{mg}/\text{kg}$ ,<sup>3</sup> classing it as a highly toxic compound by this route. It is better tolerated by mouth, 2000 ppm in the diet of rats being required to be lethal in two to three weeks. Doses below these values may be tolerated.

D. ATMOSPHERIC CONCENTRATION IMMEDIATELY HAZARDOUS TO LIFE: Unknown for man. Rabbits succumb from edema of lungs

with air concentrations of 200  $\text{mg}/\text{m}^3 \text{V}_2\text{O}_5$  after one seven-hour exposure.<sup>6</sup>

### II. Significant Properties

Vanadium pentoxide is a yellowish brown powder.

Chemical formula:  $\text{V}_2\text{O}_5$   
Molecular weight: 181.9  
Specific gravity: 3.357 ( $18^\circ\text{C}$ )  
Melting point:  $690^\circ\text{C}$   
Boiling point:  $1750^\circ\text{C}$   
Solubility: water, 0.8% by weight at  $20^\circ\text{C}$ ; soluble in alkalis.

### III. Industrial Hygiene Practice

A. RECOGNITION: At operations involved in the mining and milling of vanadium ores and in the cleaning of oil or coal-fired burners using vanadium containing fuels. Airborne vanadium pentoxide dust in concentrations above 0.5  $\text{mg}/\text{m}^3$  may cause a disagreeable sensation in the nose and throat resembling an incipient cold or effects of irritation from excessive smoking.

#### B. EVALUATION OF EXPOSURES:

- (1) *Instrumentation:* None.  
(2) *Chemical method:* Microamounts of vanadium pentoxide in the air may be determined by the method of Talvitie.<sup>8</sup>

C. RECOMMENDED CONTROL PROCEDURES: Maintain workroom exposures below 0.5  $\text{mg}/\text{m}^3 \text{V}_2\text{O}_5$ , using process ventilation, specifically designed for the operation.

### IV. Specific Procedures

A. FIRST AID (Rarely required): Remove patient from exposure, place at bed rest and call physician.

B. SPECIAL MEDICAL PROCEDURES: Any person with chronic disease of the lungs or respiratory tract should be considered unsuited for working with vanadium pentoxide. Large doses of vitamin C or calcium

EDTA have been recommended for the treatment of vanadium toxicity.<sup>3</sup> In cases of suspected over-exposure, urinary vanadium determinations may be made.<sup>9</sup> Values in excess of 30 micrograms vanadium per liter of urine are reported to be evidence of excessive exposure.<sup>4</sup>

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## XYLENE (Xylol, di-methyl benzene)

### I. Hygienic Standards

A. RECOMMENDED MAXIMUM ATMOSPHERIC CONCENTRATION (8 hours): 200 parts of vapor per million parts of air, by volume (ppm).<sup>1,2</sup>

- (1) *Basis for Recommendation*: Toxicological observations on animals, and human experience in industry.

### B. SEVERITY OF HAZARDS:

- (1) *Health*: Moderate for both acute and chronic exposures. Although xylene resembles benzene in many of its physical and chemical properties, it does not produce the chronic blood diseases characteristic of benzene absorption. Severe toxic effects which have been described from time to time have been generally attributed to the presence of impurities such as benzene. Xylene has a strong narcotic action, and its effects are noted when workers' exposures exceed 200 ppm. Dermatitis may result from repeated skin contact.
- (2) *Fire*: High. Explosive limits are 1-6% by volume in air. Flash point of o-xylene is 17°C (63°F) (closed cup).

C. SHORT EXPOSURE TOLERANCE: Narcosis in animals begins with inhalations of 2300-3500 ppm. Instances of unconsciousness in humans from severe exposures have been described, but the specific concentrations were unknown.

D. ATMOSPHERIC CONCENTRATION IMMEDIATELY HAZARDOUS TO LIFE: No fatal cases

from inhalation of vapor consisting wholly or chiefly of xylene have been recorded.<sup>4</sup> Lethal concentration for animals is about the same as for toluene (1,600 ppm) but less than benzene (2,440 ppm).<sup>3</sup>

### II. Significant Properties

Xylene is a colorless, flammable liquid with an odor similar to toluene. Commercial xylene is primarily a mixture of o-, m-, and p-xylene (1,2-, 1, 3- and 1, 4-dimethyl benzene) having a boiling range from about 127°C to 159°C, (261-319°F.).

The meta-isomer is generally the principal component and its properties are given below.

Chemical formula:  $C_6H_4 (CH_3)_2$

Molecular weight: 106

Specific gravity: 0.864 (20°C)

(Commercial product does not differ significantly from this value)

Boiling point: 139.1°C (For boiling range of commercial product, see above)

Relative vapor density: 3.66 (air = 1)

Vapor pressure: 10 mm Hg at 32.1°C

Solubility: Insoluble in water; miscible in alcohol, ether, and many common organic solvents.

At 25°C and 760 mm Hg,

1 ppm of vapor: .00376 mg/liter

1 mg/liter: 266 ppm



### III. Industrial Hygiene Practice

A. **RECOGNITION:** May be recognized by its characteristic odor which resembles that of toluene and, more remotely, benzene. The commercial solvent may contain substantial quantities of benzene. Xylene is used as the starting point for the manufacture of many dyes and organic chemicals and as a solvent for gums and oils.

B. **EVALUATION OF EXPOSURES:** (There is no common test specific for xylene; benzene, toluene and other aromatic hydrocarbons interfere).

- (1) *Instrumentation:* Direct determination by the use of the Aromatic Hydrocarbon Detector (Mine Safety Appliances Company, Pittsburgh 8); the Dräger Gas Detector (Drägerwerk, Lübeck, Germany); the Davis Vaportester Model M-6 (Davis Emergency Equipment Company, Newark, N. J.); or the MSA Combustible Gas Detector, Model 40.
- (2) *Chemical Method:* Collection in fuming nitric acid with gas absorber, or as grab sample of 200-300 ml in glass gas sampling flask and then nitrating with fuming acid. The nitrated xylene is extracted with butanone and the

color compared with standards.<sup>5</sup> Benzene and toluene interfere. Other methods described in Benzene Hygienic Guide may also be used.

C. **RECOMMENDED CONTROL MEASURES:** Maintain workroom atmospheres below 200 ppm by means of process enclosure and/or ventilation. Prevent contact with the liquid through the use of protective clothing and chemical-type goggles.

### IV. Specific Procedures

A. **FIRST AID:** Remove from exposure; remove contaminated clothing, cleanse skin, eyes, etc. Artificial respiration should be started immediately if breathing has stopped.

B. **SPECIFIC MEDICAL PROCEDURES:**

- (1) *Preplacement:* Complete clinical and laboratory examinations are desirable for proper placement.
- (2) *Periodic:* Clinical and laboratory studies should be done.

### V. Literature References

1. American Conference of Governmental Industrial Hygienists: *AMA Arch. Ind. Health*, 14:187, 1956.
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## ETHYLENE GLYCOL MONOMETHYL ETHER

### I. Hygienic Standards

A. **RECOMMENDED MAXIMUM ATMOSPHERIC CONCENTRATION** (8 hours): 25 parts of vapor per million parts of air, by volume (ppm).<sup>1</sup>

- (1) *Basis for Recommendation:* Human experience.<sup>3</sup>

B. **SEVERITY OF HAZARDS:**

- (1) *Health:* Moderate, for chronic exposures; low, for acute. Severe anemia and neurological symptoms were observed in workers exposed one month or more.<sup>4,5</sup> Animal studies confirmed the blood changes, but relatively high concentrations (800 ppm) were used.<sup>7</sup> Probably because of its low volatility, only a few cases of illness have been attributed

to the compound. Because of its not unpleasant odor and its lack of irritant properties, potentially harmful concentrations may be tolerated for rather prolonged periods of time without discomfort.

- (2) *Fire:* Low. Flash point is 42°C (107°F) (closed cup).

C. **SHORT EXPOSURE TOLERANCE:** 800 ppm produced no deaths in mice in seven hours.<sup>6</sup>

D. **ATMOSPHERIC CONCENTRATION IMMEDIATELY HAZARDOUS TO LIFE:** Unknown.

### II. Significant Properties

Ethylene glycol monomethyl ether is a colorless liquid with a slight odor. One of the common trade names of this compound is methyl cellosolve.

Chemical formula:  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$   
 Molecular weight: 76  
 Specific gravity: 0.966 (20°C)  
 Boiling point: 124.6°C  
 Relative vapor density: 2.62 (air = 1)  
 Vapor pressure: 6 mm Hg at 20°C  
 Solubility: Soluble in water and most organic solvents.

At 25°C and  
 760 mm Hg,  
 1 ppm of vapor: 0.00312 mg/l  
 1 mg/liter of  
 vapor: 321 ppm

### III. Industrial Hygiene Practice

A. RECOGNITION: Used as a solvent for cellulose esters, in lacquers, and in the plastics industry.

#### B. EVALUATION OF EXPOSURES:

- (1) *Instrumentation*: None.
- (2) *Chemical*: Absorption in water, followed by dichromate oxidation. Not specific, but interfer-

ence of some common solvents can be eliminated by special procedures.<sup>2</sup>

C. RECOMMENDED CONTROL PROCEDURES: Maintain workroom atmospheric concentration below 25 ppm by process or general ventilation.

### IV. Specific Procedures

A. FIRST AID: Usually not applicable.

B. SPECIAL MEDICAL PROCEDURES: (Including preplacement) Clinical and laboratory examinations are desirable.

### V. Literature References

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6. WERNER, HAROLD W., et al: *J. Ind. Hyg. & Tox.*, 25:157, 1943.
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## PHOSPHORIC ACID

### I. Hygienic Standards

A. RECOMMENDED MAXIMUM ATMOSPHERIC CONCENTRATION (8 hours): Based upon comparable experience and data for sulfuric acid,<sup>2,3</sup> it is believed that a level of one milligram of  $\text{H}_3\text{PO}_4$  per cubic meter of air ( $\text{mg}/\text{m}^3$ ) is safe. Mist exposures should be kept below the level causing discomfort, or irritation to the eyes, or respiratory tract.

- (1) *Basis for Recommendation*: Human experience in industry.

#### B. SEVERITY OF HAZARDS:

- (1) *Health*: Moderate, for both chronic and acute exposures. Effects are primarily irritation of mucous membranes and skin. It is not as hazardous in this respect as either nitric or sulfuric acids. 75% phosphoric acid will cause destruction of body tissues and severe burns.<sup>2</sup>
- (2) *Fire*: None (hydrogen gas may be generated with certain metals).

C. SHORT EXPOSURE TOLERANCE: Unknown.

D. ATMOSPHERIC CONCENTRATION IMMEDIATELY HAZARDOUS TO LIFE: Unknown.

### II. Significant Properties

A corrosive, mineral acid. The generally encountered tribasic acid, orthophosphoric acid, occurs as colorless crystals readily soluble in water. Available commercially in various strengths, usually as 50%, 75% and 85% aqueous solutions.

Chemical formula:  $\text{H}_3\text{PO}_4$

Molecular weight: 98

Specific gravity: 1.834 (18°C)

Specific gravity of

85% Solution: 1.685 (at 25°C)

Solubility: In alcohol or water

Vapor pressure

(85% aqueous

solution):

2.16 mm Hg at 20°C

### III. Industrial Hygiene Practice

A. RECOGNITION: By its irritating effects to the skin, eyes, and respiratory tract. Major uses are in agriculture, soft drinks, food, chemicals, and in the manufacture of phosphate salts.

**B. EVALUATION OF EXPOSURES:**

- (1) *Instrumentation*: No direct reading instruments available.
- (2) *Chemical method*: Collection by impinger or sintered absorber in sodium hydroxide solution, followed by titration of free acid.

**C. RECOMMENDED CONTROL PROCEDURES:**

Protective goggles and clothing should be worn to prevent direct contact with the acid. If large-scale contamination of the body is likely, safety showers should be located nearby. Eye wash fountains should be close to use sites. Exhaust ventilation or acid gas canister masks may be necessary in confined spaces, or at elevated temperatures.

**IV. Specific Procedures**

**A. FIRST AID:** Remove clothing and flush surface areas with large amounts of water if skin contact has been severe. Eyes should be irrigated with large amounts of water for 15 minutes. Medical attention should be secured at once.

**B. SPECIAL MEDICAL PROCEDURES** (including preplacement): None.<sup>1</sup>

**V. Literature References**

1. American Petroleum Institute: Toxicological Review, Phosphoric acids, New York, 1953.
2. GARRETT, J. T. (Monsanto Chemical Co.): Personal communication.
3. Manufacturing Chemists' Association: Chemical Safety Data Sheet: Phosphoric Anhydride.
4. Monsanto Chemical Company: The Handling of 75% Phosphoric Acid in Tank Car Quantities.

**TOLUENE (Toluol, Methyl Benzene)****I. Hygienic Standards**

**A. RECOMMENDED MAXIMUM ATMOSPHERIC CONCENTRATION** (8 hours): 200 parts of vapor per million parts of air, by volume (ppm).<sup>1,2</sup>

- (1) *Basis for Recommendation*: Toxicological observations on animals and human experience in industry.

**B. SEVERITY OF HAZARDS:**

- (1) *Health*: Moderate for acute and chronic exposures. Although toluene resembles benzene in many of its physical and chemical properties, it does not produce the chronic blood diseases characteristic of benzene absorption. Toluene has a strong narcotic action, and effects are noted when workers' exposure exceeds 200 ppm. Dermatitis may result from repeated skin contact.<sup>4,5</sup>
- (2) *Fire*: High. Explosive limits are 1.27 to 6.75%. Flash point is 4°C (40°F) (closed cup).

**C. SHORT EXPOSURE TOLERANCE:** In experimental subjects 600 ppm produced extreme fatigue, mental confusion, exhilaration, nausea, headache and dizziness after three hours.<sup>4</sup>

**D. ATMOSPHERIC CONCENTRATION IMMEDIATELY HAZARDOUS TO LIFE:** 8,000-12,000 ppm rapidly fatal to mice;<sup>3</sup> no comparable data on humans.

**II. Significant Properties**

Toluene is a colorless, flammable liquid with an odor similar to benzene.

Chemical formula:  $C_6H_5CH_3$

Molecular weight: 92

Specific gravity: 0.867 (20°C/4°C)  
(Commercial product: 0.86-0.87)

Boiling point: 110.6°C (Commercial product: 109-111°C)

Relative vapor density: 3.2 (air = 1)

Vapor pressure: 30 mm Hg at 26°C

Solubility: Miscible with most organic solvents

At 25°C and 760 mm Hg,  
1 ppm of vapor: 0.00376 mg/liter  
1 mg/liter of vapor: 266 ppm

**III. Industrial Hygiene Practice**

**A. RECOGNITION:** By its benzene-like odor. The commercial solvent may contain substantial quantities of benzene and/or xylene. Toluene is used extensively as the starting point for the manufacture of many important organic chemicals such as explosives and dyes, and as a solvent for a wide variety of gums, resins, and fats. It is also used as a diluent in cellulose ester lacquers.

**B. EVALUATION OF EXPOSURES:**

- (1) *Instrumentation*: Direct determination by the use of the Aromatic Hydrocarbon Detector (Mine Safety Appliances Company, Pittsburgh 8); Dräger Gas Detector (Drägerwerk, Lübeck, Germany); the Davis Vapometer Model M-6 (Davis Emergency Equipment Company, Newark, N. J.); or the MSA Combustible Gas Detector, Model 40.

- (2) *Chemical Method*: Collection in fuming nitric acid with gas absorber, or as grab sample of 200-300 ml in glass sampling flask, followed by nitration, butanone extraction, and colorimetry.<sup>6</sup> Benzene and xylene interfere. Methods described in Benzene Guide may also be used.

**C. RECOMMENDED CONTROL MEASURES:** Maintain workroom atmosphere below 200 ppm by means of process enclosure and/or ventilation. Prevent contact with the liquid through the use of protective clothing and chemical-type goggles.

*Because of space limitations, it is impossible to list all methods of exposure evaluation. The selections have been made on the basis of current usage, reliability, and applicability to the usual industrial type of exposure. Any specific evaluation and/or control problem will involve professional judgment. This can best be done by professional industrial hygiene personnel.*

*Respiratory protective devices are commercially available. Their use, however, should be confined to emergency or intermittent exposures and not relied upon as primary means of hazard control.*

*A relative scale is used for rating the severity of hazards: nil, low, moderate, high, and extra hazardous.*

#### HYGIENIC GUIDES COMMITTEE

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#### IV. Specific Procedures

**A. FIRST AID:** Remove from exposure; remove contaminated clothing, cleanse skin, eyes, etc. Artificial respiration should be started at once if breathing has stopped.

##### B. SPECIFIC MEDICAL PROCEDURES:

- (1) *Preplacement*: Complete clinical and laboratory examinations are desirable for proper placement.
- (2) *Periodic*: Clinical and laboratory studies should be done. Absorption of toluene results in an increase in the amount of hippuric acid in the urine. This has been suggested as an exposure index.<sup>4</sup>

#### V. Literature References

1. American Conference of Governmental Industrial Hygienists: *AMA Arch. Ind. Health*, 14:187, 1956.
2. American Standards Association: *American Standard Z37.12-1943*.
3. LAZAREW, N. W.: *Arch. Exptl. Path. Pharmacol.*, 143:223, 1929.
4. VON OETTINGEN, W. F., et al: *Pub. Health Bull.* 279, Superintendent of Documents, Washington, D. C., 1942.
5. WILSON, R. H.: *J.A.M.A.*, 123:1106, 1943.
6. YANT, W. P., et al: *Report of Investigation #3323*. U. S. Bureau of Mines, 1936.

### Hygienic Guides and Binders Available

**I**NDIVIDUAL Hygienic Guides in loose-leaf form may be obtained from the American Industrial Hygiene Association, 14125 Prevost, Detroit 27, Michigan, at 25c each. Discount of 20% allowed on orders of five or more; 40% on orders of 100 or more. Also available are flexible loose-leaf binders for the individual Hygienic Guide sheets. The binders have been especially designed to provide maximum protection and ease of handling of the Guides. They will be particularly useful in keeping a permanent file. The binders are blue in color, with white lettering, and are fitted with  $\frac{3}{4}$ " rings. The price is \$1.25. The Guides and the binders may be ordered on the blank on page 155.

## ◆ News of the Local Sections

### Chicago

MAREN A. STANLEY, R.N., Administrative Supervisor of the Chicago Medical Department of Union Carbide and Carbon Corporation, spoke at the March meeting of the Chicago Section on "The Industrial Nurse—Her Place on the Occupational Health Team." Also at the March meeting officers for 1957-58 were elected. They are: President-Elect, PAUL J. WHITAKER, M.D.; Secretary-Treasurer, ALBERT EDWARDS; Directors for three year term, FRANK P. MUELLER, PAULINE PRYOR, R.N., THEODORE F. WICKORD, HAROLD W. WISTRAND; Director for two year unexpired term, PAUL D. HALLEY; Director for one year unexpired term, LOUIS X. KAREL.

At the April meeting, HOWARD N. SCHULZ, Industrial Hygienist, Abbott Laboratories, spoke on "Industrial Hygiene Experience in the Drug Industry."

### Northern California

NEW OFFICERS elected are as follows: President-Elect, CHRISTINE EINERT, M.D., Executive Committee, JACK WASHKUH; Secretary-Treasurer, WESLEY J. ROBERTS.

The Northern California Section has established on behalf of DR. ROBERT T. LEGGE, pioneer industrial physician in Northern California, the Robert T. Legge Testimonial Award. The award is to be in the form of a textbook related to occupational health and is to be given each year to a student from each of the following schools: Stanford Medical School, University of California Medical School and University of California School of Public Health.

The 46th meeting of the Section was held at the San Francisco Naval Shipyard on March 19, attended by 62 members and guests. The guest from the greatest distance was DR. G. HUMEETHE from Thailand. The program included the presentation of three papers scheduled to be given by members at the Industrial Health Conference in St. Louis. They were: "Hydrocarbon Synthesis in Combustion - Liquid Fuels," by BERNARD TEBBENS, SC.D.; "Evaluation of Carcinogenic Potency of Two Representative Diepoxy Resins," by CHARLES H. HINE, M.D.; "Decontamination of Synthetic Radio-

active Fall-out from the Intact Human Skin," by WILLIAM J. FRIEDMAN.

At the meeting held May 14, the report of delegates to the St. Louis meeting was presented, after which E. C. EVANS, III, U. S. Naval Radiological Defense Laboratory, addressed the group on "An Electrostatic Fog Precipitator," and R. R. NEWELL, M.D., Stanford University, on "Permissible Radiation Dose - Is O.l.r Per Week Inadvisable?"

### Southern California

WILLIAM FRANK, Operations Officer, Los Angeles Office of Civil Defense, spoke to the Southern California Section March 14, on the subject of "Industry Participation in Civil Defense Planning." MR. FRANK brought the group up to date on progression of plans. JOSH ROGERS, Director of Occupational Health, Los Angeles City Health Department, and RICHARD K. DICKEY, Chief of the Radiological Defense Division, Los Angeles Office of Civil Defense, also discussed various phases of the subject.

At the May 9, meeting, A. A. JARRETT, Atomic International Division of North American Aviation, Inc., spoke on "Radiation Engineering as a Field in Industrial Hygiene." MR. JARRETT discussed the industrial hygiene problems associated with the Sodium Reactor Experiment in the Santa Susana Mountains near Los Angeles.

### Western New York

ON FEBRUARY 18, we held a joint meeting with the Rochester Chapter of the American Chemical Society. DR. JAMES H. STERNER, Medical Director, Eastman Kodak Company, spoke on "Health in the Chemical Industry."

On March 27, PROFESSOR LUCIEN DAUTREBANDE, of Belgium, spoke on "Aerosols in Industrial Hygiene." PROFESSOR DAUTREBANDE is currently at the University of Rochester under a Public Health Fellowship Grant. Also, new officers for 1957-58 were installed. They are: President, WILFRED L. MCMAHON; President-Elect, FRANKLIN A. MILLER; Secretary-Treasurer, J. BARRIE GRAHAM; Directors, ROBERT H. WILSON, SANFORD I. HARTWELL, DR. PAUL E. MORROW.



